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JOINING OF MOLYBDENUM

WILLIAM N. PLATTE

WESTINGHOUSE RESEARCH LABORATORIES

NOVEMBER 1956

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WADC TECHNICAL REPORT 54-17

PART 3

ASTIA DOCUMENT No. AD 110570

JOINING OF MOLYBDENUM

WILLIAM N. PLATTE

WESTINGHOUSE RESEARCH LABORATORIES

NOVEMBER 1956

MATERIALS LABORATORY
CONTRACT No. AF 18(600)-114
PROJECT No. 1252

WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

FOREWORD

This report was prepared by the Westinghouse Research Laboratories under USAF Contract AF 18(600)-1114. This contract was initiated under Project No. 1252, Task No. 73022, "Production of Sound Joints in Molybdenum," and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Lt T. Hikido and Lt R. J. Campbell acting as project engineers.

This report covers work conducted from January 1955 to February 1956.

ABSTRACT

The use of welding atmospheres of purified argon and helium is shown to cause very little contamination of the weld metal in molybdenum fusion welds. However, the use of high purity atmospheres provides only a small improvement in ductility over welds made in welding grade argon.

Increasing the carbon content of the base material within the range 0.04% to 0.06% appears to improve the ductility of the weld metal. Additions of 0.5% titanium in the presence of 0.05% carbon gave welds which could be deflected 120° at 80°F. Increasing the carbon content from 0.015 to 0.05% improved the ductility of the molybdenum welds containing 0.5% titanium. Additions of 0.16% aluminum to the molybdenum yielded welds which could be deflected 120° at 120°F.

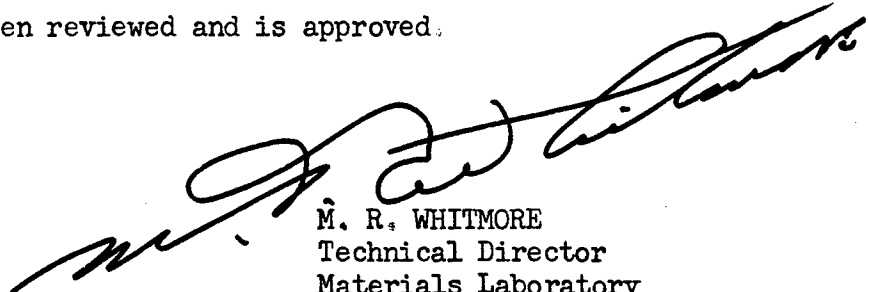
Exploratory studies on the effectiveness of diffusion as a method of removal of nitrogen from the weld metal are discussed. The use of thermal treatment as a method of improving mechanical properties by over-aging and polygonization was explored. Weld metal additions are also discussed briefly. The use of Ti and Zr as deoxidizers in vacuum sintered molybdenum is described.

An exploration into the effects of residual welding stresses showed that the weld crater cracking encountered in many cases is caused by measurable stresses in the region of the weld which approximate the rupture strength of the material.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER



M. R. WHITMORE
Technical Director
Materials Laboratory
Directorate of Research

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JOINING OF MOLYBDENUM*

I INTRODUCTION

Molybdenum joints made by the fusion welding method are subject to porosity, hot cracking, and loss of ductility near ambient temperature. During the past three years several phases of these problems have been studied. The investigations have shown that the primary cause of porosity in the weld metal is the presence of gases in the parent metal. This type of defect can be eliminated by deoxidization of the base plate. The principles of deoxidization apply to both arc-cast and sintered materials.^{1,2}

Weld cracking at elevated temperatures has been related both to the deoxidization practice of the molybdenum and the oxygen in the welding atmosphere.^{1,2} The ductility of the weld metal has been shown to be a function of the oxygen, nitrogen and possibly the carbon contents. Oxygen and nitrogen contamination of the weld metal is caused by the presence of these elements in the base plate and in the welding atmosphere. Carbon is frequently used as a deoxidizing element in the base plate and hence is found in the weld metal. Studies reported earlier indicated that if suitable ductility is to be obtained, the interstitial elements, oxygen and nitrogen, must be held to minimum values in the weld metal.² This means close control of all the sources of these interstitial elements.

The effort during the past year has been directed toward control of the ductility by reducing these interstitial elements through control of the welding atmosphere, changes in the parent plate, post-weld diffusion treatment, and aging of the weld metal to reduce the effectiveness of precipitates on the ductility. The principal source of weld contamination by oxygen and nitrogen is the welding atmosphere.^{1,2} Atmospheres of the necessary order of purity require that the inert gases commercially

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available be repurified just prior to welding. Commercial welding grade argon may contain as much as 0.05% oxygen and 0.1% nitrogen. This gas is water pumped and contains large amounts of water vapor. Previous work has indicated that the oxygen limit for welds of reasonable ductility is 0.005% in the welding atmosphere.² Nitrogen must also be reduced much below 0.1% if good ductility is to be obtained.

Commercial helium may have sufficient purity to meet some of the welding requirements but earlier work indicates that this grade of gas is not dependable. Some welds were made using a select grade of charcoal purified helium. However, this gas could not be used successfully in the chamber available. The difficulty appeared to be caused by stratification of the impurity gases at the bottom of the chamber. Helium, being lighter, could not be used successfully to purge the chamber. Argon was much more successful because it is heavier than the impurity gases.

Gas purification systems were made to purify either argon or helium. Two methods were tried. Molten lithium was used first without success. However, a unit using a cold trap plus P_2O_5 , followed by hot Zr, proved to be successful in obtaining argon of high purity. This system reduced the oxygen and nitrogen in the argon below detectable limits for the mass spectrometer.

Removal of contaminating gases from the weld zone by diffusion into the base plate has been investigated. Preliminary calculations showed that nitrogen could be removed at temperatures at or above 1000°C. Oxygen required at least 2000°C for diffusion in molybdenum. Weld test plates were made and the degree of diffusion determined. Extraneous masking effects tended to confuse the diffusion results so that their interpretation was difficult.

Molybdenum deoxidized by means other than carbon was examined through weld and bend ductility tests. Titanium and aluminum deoxidized arc-cast material was used in these tests in an attempt to show the effectiveness of deoxidizer additions other than carbon. This field

of investigation seemed to be the most fruitful since welds were obtained in titanium deoxidized molybdenum which could be deflected 120° at 80°F, and in the aluminum deoxidized arc-cast molybdenum the welds were deflected 120° at 120°F. Carbon deoxidized material requires temperatures of 200 to 300°F in order to sustain this degree of bending.

During the course of this year's investigations the problem of weld crater cracking was encountered. Cracking through the weld crater occurred when the test plate had cooled to ambient or near ambient temperatures. This cracking sometimes occurred minutes after welding but could require as long as three weeks. Cracking often occurred with considerable violence. In some cases the section at the end of the weld bead would be moved as far as 18". The cause of this type of failure was studied from the point of view of material composition, since one lot of material seemed more prone to this type failure than the other. However, chemical analyses showed very little difference in the composition of the material. Strain gage measurements made on a weld which did not crack indicated that the difficulty was primarily due to residual welding stresses in the area near the weld crater. The crater cracking appeared to be due to a borderline strength condition which could be sensitive to small differences in composition or residual rolling strains.

Exploratory investigations were made in the field of post-weld heat treatment to observe the effect of aging on precipitates found in the weld metal. It was believed possible that precipitates in the weld metal could be overaged and the ductility of the weld material improved. The data indicated that this field should be examined further. Post-weld straining at an elevated temperature and subsequent heat treatment were tried in an attempt to promote polygonization. It was believed that a polygonized structure in the weld metal could improve the ductility by means of a fine grain effect. Unfortunately, there was insufficient time to complete this phase of the investigation.

A small amount of work was done using vacuum sintered molybdenum. This work centered around development of deoxidization techniques. It was found earlier^{1,2} that sintered molybdenum could not be welded unless suitable deoxidizers were added using the proper technique. Previously, Ti was the only deoxidizer which showed any degree of success. However, during this report period, Zr was used and was moderately successful. New techniques for addition of Ti as a deoxidizer to powder metallurgy molybdenum were tried. The objective of the changes in the deoxidization method was to improve the uniformity of the material. However, the results indicated that additions of Ti are best made with the titanium powder wet in spite of the mixing difficulties.

II EQUIPMENT DEVELOPMENT AND IMPROVEMENT

Previous exploratory work on the use of getters in the welding atmosphere supply lines was described in the Second Annual Report on Joining of Molybdenum.² The early studies involved the use of hot titanium chips in the incoming gas lines of the welding chamber. The welding chamber, Fig. 1, was originally designed for use with a continuous flow of gas at the rate of 27.5 cu ft/hr. This arrangement required the use of 10 to 14 cu ft of gas during the purge and welding periods. Purification of this amount of gas at the flow rates involved and to the purity required is difficult. A small tube furnace filled with hot titanium chips and heated to 816°C was tried and the results were described in a previous report.² Visual examination of the chips after welding indicated that the gettering ability of the purification train was probably exhausted before welding had been completed. This condition was the result of two

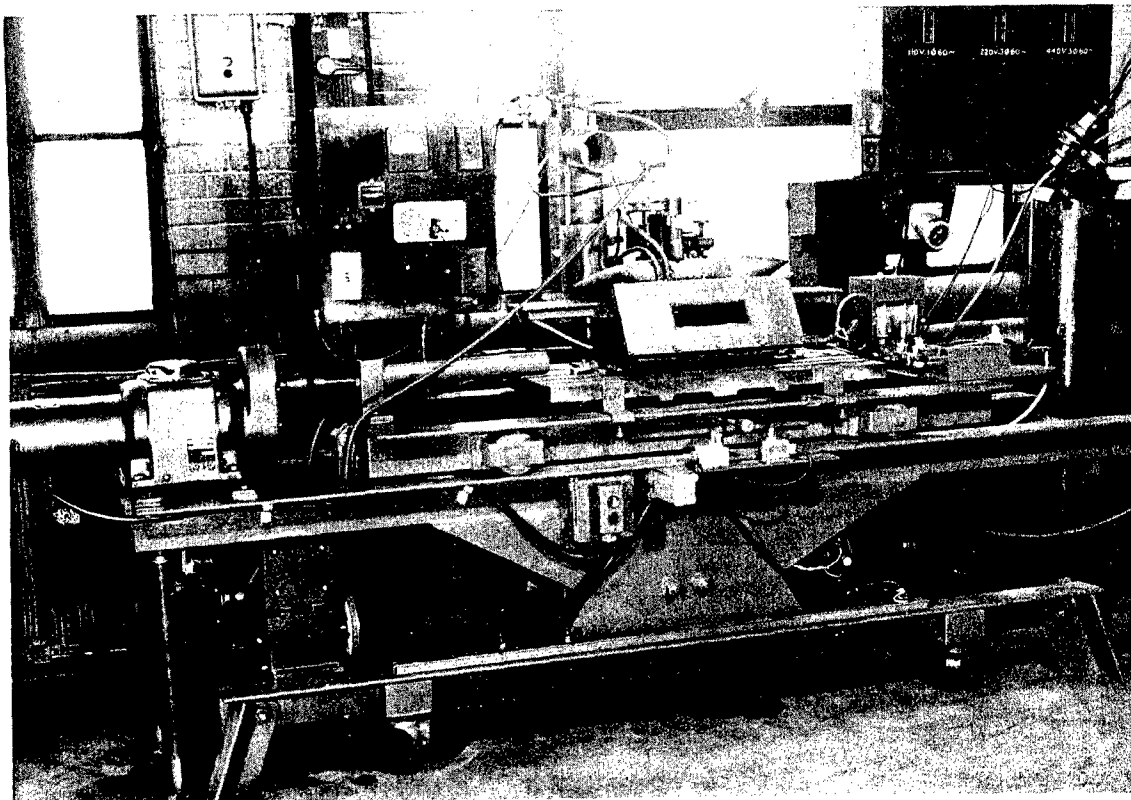


Fig. 1 - Welding Chamber

factors: (1) the hot zone in the furnace used was too short; (2) the welding chamber as operated required an excessive amount of gas.

A. Welding Chamber

In order to reduce the amount of purified inert gas required during purging and welding, the welding chamber was modified so that it would hold a fixed positive pressure for an extended period of time. This was accomplished by relatively minor changes in the control and gas supply units. The chamber was altered so that after purging

with commercially available inert gas had been completed, the gas in the chamber could be purified using a suitable system. This modification required a pump in the gas supply lines so connected that the external gas supply could be stopped and the gas in the chamber circulated through the purification unit. A Sigma (R) pump was used to accomplish the circulation of the gas. This pump does not disrupt the gas line at any point and there is no possibility of contamination of the gas by the pumping action. The arrangement of the welding chamber, gas supply, purification train, and gas sampling equipment is shown in a schematic drawing, Fig. 2. The

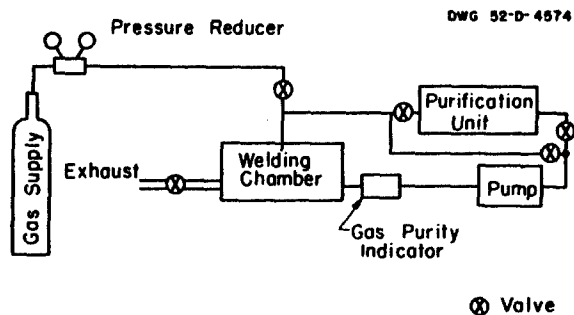


Fig. 2 - Modified Gas Supply System

arrangement of the purification system will be discussed in a later section.

B. Purification Systems

Exploratory work on gas purification, reported in the Second Annual Report, Joining of Molybdenum,² was done using a one-inch tube furnace with a five-inch hot zone. Titanium chips were used at 816°C. In the exploratory work, the chamber was purged using commercial helium or argon with the purification furnace bypassed. After purging, the purification furnace was placed in the incoming gas line and the purging operation was cycled four times. The gas was also purified during the actual welding operation. Visual examination of the titanium chips after welding indicated that the gettering action of the system was probably expended before the welding operation had started. Analyses of the welding atmospheres using mass spectrometric techniques showed no difference in the purity as compared with unpurified gas. The lack of improvement of the atmosphere was attributed to the inadequate purification train and the

inability of the mass spectrometer to detect oxygen and nitrogen in amounts below 0.02%. With these observations as a basis, work was done both to improve the purification train and to devise a method of atmosphere purity indication which would be sufficiently sensitive to detect impurities of the orders of magnitude required for molybdenum welding applications. It was shown in a previous report² that the oxygen contamination in the welding atmosphere must be $<0.005\%$.

The use of molten lithium was suggested³ as a gettering material for oxygen, nitrogen and water vapor. Preliminary investigations indicated that this material should be successful since, in the molten state between 186°C and 700°C , the liquid lithium reacts readily with the impurity gases involved but does not have a sufficiently

high vapor pressure to cause contamination of the atmosphere with lithium. The available data indicated that the products of reactions with oxygen and nitrogen were also stable at these temperatures. An experimental unit was constructed based on these data.

The simplest way to produce the desired reactions was to bubble the welding atmosphere through the molten lithium. This was accomplished with an iron pot one inch in diameter and a lithium depth of approximately three inches. The lithium was maintained at $200\text{--}220^{\circ}\text{C}$. The lithium pot with the inlet pipe and exhaust heat exchanger is shown in Fig. 3. The cold gas enters through the center tube and is preheated by the exit gas. This arrangement is intended

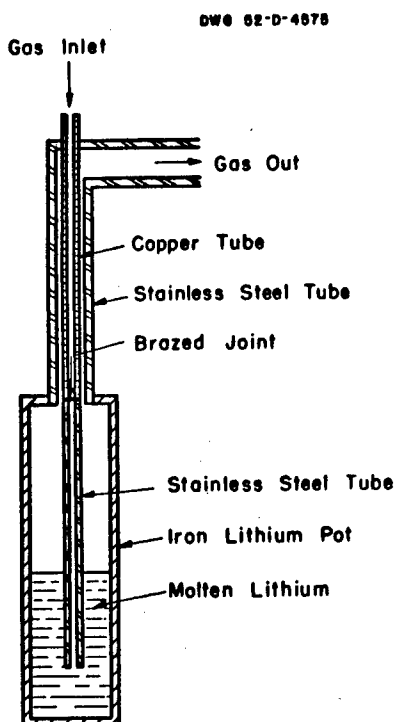


Fig. 3 - Gas Purifier and Heat Exchanger to prevent excessive heat loss in the furnace and possible solidification of the lithium.

Difficulties were experienced in preparing the lithium and filling the chamber. It was difficult to keep the lithium in an uncontaminated condition until it could be melted under an inert gas atmosphere. Freshly cut lithium tarnishes very rapidly in air. This is especially true if the humidity is high. It was not possible to keep the material bright, even under oil, until all the old surfaces could be removed. However, it was found that the lithium could be pickled in absolute ethyl alcohol for a few seconds and then stored in a bath of absolute ethyl alcohol and dry ice. The lithium was exposed to air for only a short time while the furnace was being filled. Heating was accomplished under an argon atmosphere. White fumes were evident in the exhaust gases from the lithium pot and these fumes continued even after the lithium was molten.

The lithium gettering unit was tried using argon at a flow rate of 3 to 10 cu ft/hr. The lithium was heated to 210°C. The trial run was unsuccessful. Apparently lithium oxide or hydroxide was formed as a fine powder and carried out into the outgoing atmosphere. This condition cannot be tolerated because of contamination of the molybdenum weld metal with oxides or hydroxides of lithium. Use of the molten lithium method of oxygen, nitrogen and water vapor removal has been suspended in favor of other less difficult procedures which have been established at the Westinghouse Research Laboratories.

Work on a separate Westinghouse project of an unrelated nature had been instrumental in the development of a helium purification unit.⁴ This system had been found to be capable of producing helium with oxygen concentrations of less than 10^{-10} mm partial pressure. Gas of this purity is better than the estimated required purity for welding work, 0.005% O_2 . The purification system will also reduce the nitrogen, water vapor and hydrocarbons to very low limits. Data on these gases are not available. The purification system is shown

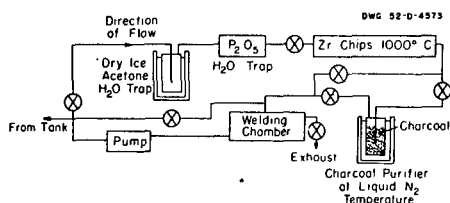


Fig. 4 - Helium Purification System for Welding Atmosphere

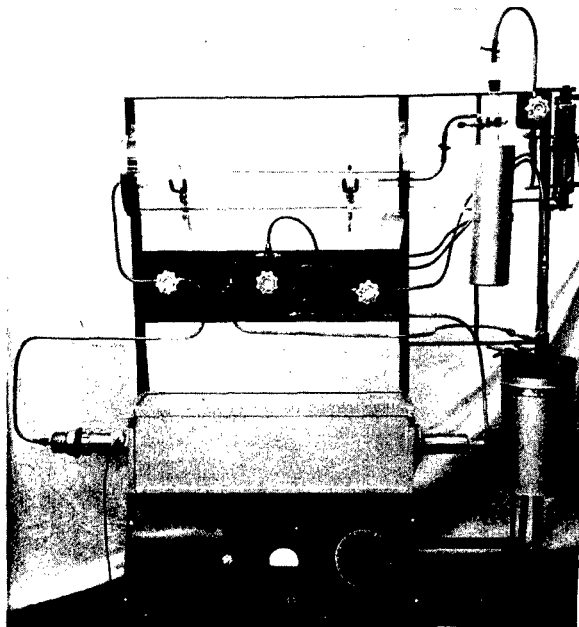


Fig. 5 - R-14273 - Helium and Argon Purification Unit

schematically in Fig. 4. The system consists of a dry ice acetone trap for water vapor followed by a tube containing P_2O_5 to further strip the atmosphere of water. Hot zirconium ($900^\circ C$) is used to remove oxygen and nitrogen. When helium is used a charcoal adsorption unit at liquid nitrogen temperatures will act as a final stripper for the impurity gases and hydrocarbons. However, when argon is used the liquid nitrogen adsorption unit cannot be used because of the small difference in the boiling points of nitrogen and argon. Nitrogen boils at $-195.8^\circ C$. Argon boils at $-185.7^\circ C$ and freezes at $-189.2^\circ C$. It is obvious that the argon would be frozen by a liquid nitrogen trap. Hence,

for use with argon the charcoal adsorption unit is by-passed. The assembled purification unit is shown in Fig. 5. This unit has been operated at a gas flow of 2 to 3 cu ft/hr and the output gases have been used in welding applications. Mass spectrometer readings of welding atmospheres obtained with this unit show that the concentrations of oxygen, nitrogen and water vapor are, in general, below the lower limit of the sensitivity of the mass spectrometer. The limit on the mass spectrometric equipment available is 0.02%. Chemical analyses

of weld beads made under the purified atmospheres show that the amount of oxygen acquired by the weld bead during welding was 0.001% greater than that of the unwelded material. This difference is within the limits of accuracy of the analysis technique.

In order to obtain these results the welding chamber was purged with tank grade argon in a manner which had been shown to produce an atmosphere in the chamber equivalent to the gas in the tank. Each of the purging operations, of which there are thirty, consists of filling the chamber and expansion unit, Fig. 1, with argon and then pumping the gas from the expansion unit. During this stage of the purging operation the argon flow into the welding chamber is 27.5 cu ft/hr and the purification unit is by-passed. After the welding chamber contains an atmosphere of tank grade argon, the flow rate is reduced to 2 to 3 cu ft/hr and all the gas is passed through the purification unit. During this second stage, the chamber is again purged for a ten cycle purge series using the purified argon and the same general refill and pump-out procedures used before, except that a flow rate of 2-3 cu ft/hr is used. After the second stage of purging is completed the pressure in the chamber is increased to approximately 30 mm of Hg and maintained at this pressure for 45 minutes while the gas in the chamber is recirculated through the purification unit at about 2 to 3 cu ft/hr. It is at this stage that the weld is made and the gas samples taken which show the low impurity contents.

C. Gas Purity Indicator

Welding atmospheres of the purity discussed in the previous section require special means of analysis or purity indication. The mass spectrometric methods used in earlier investigations are not

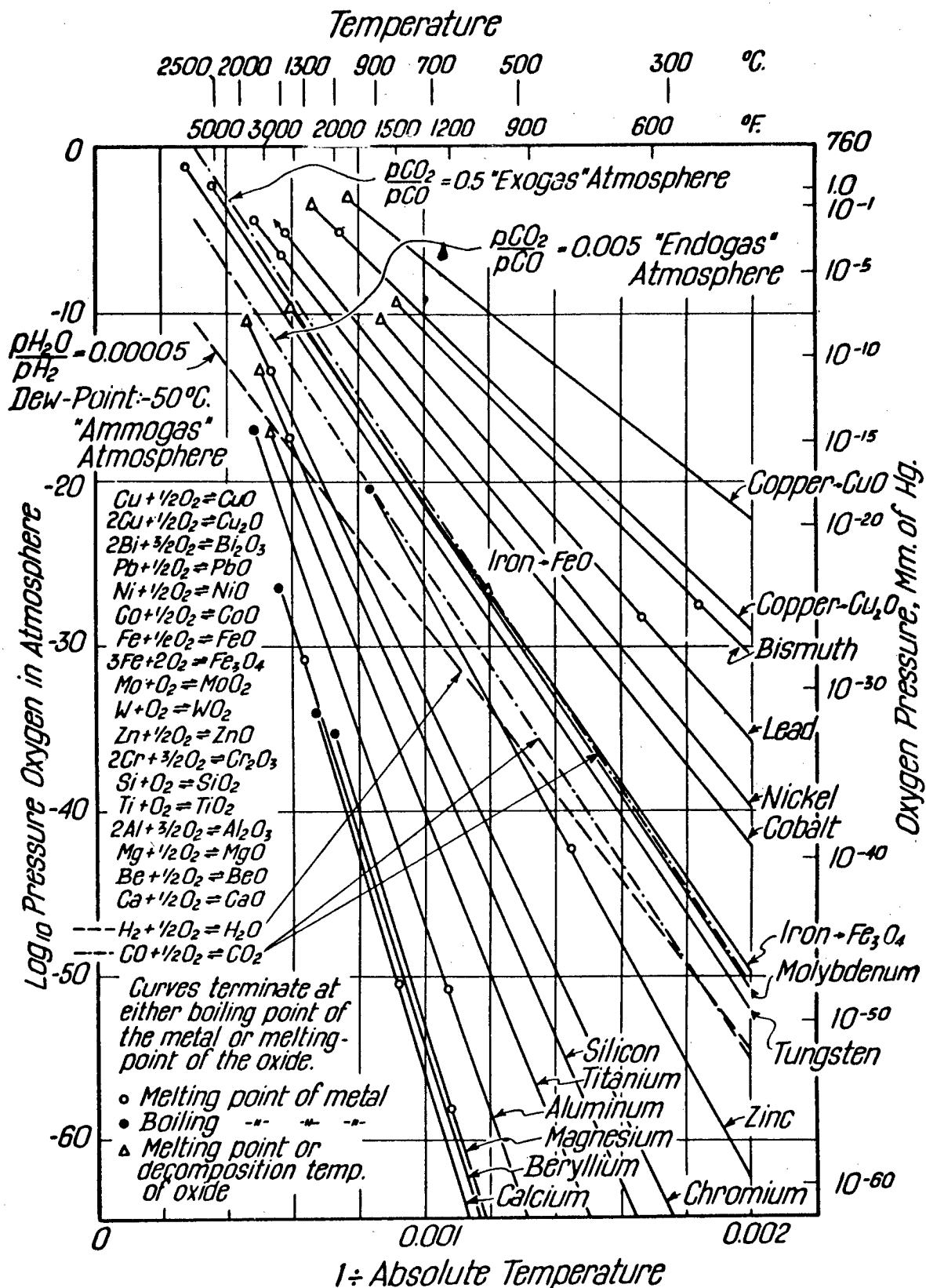


Fig. 6 - Dissociation Pressures of Metal Oxides Formed on Their Solid Metals

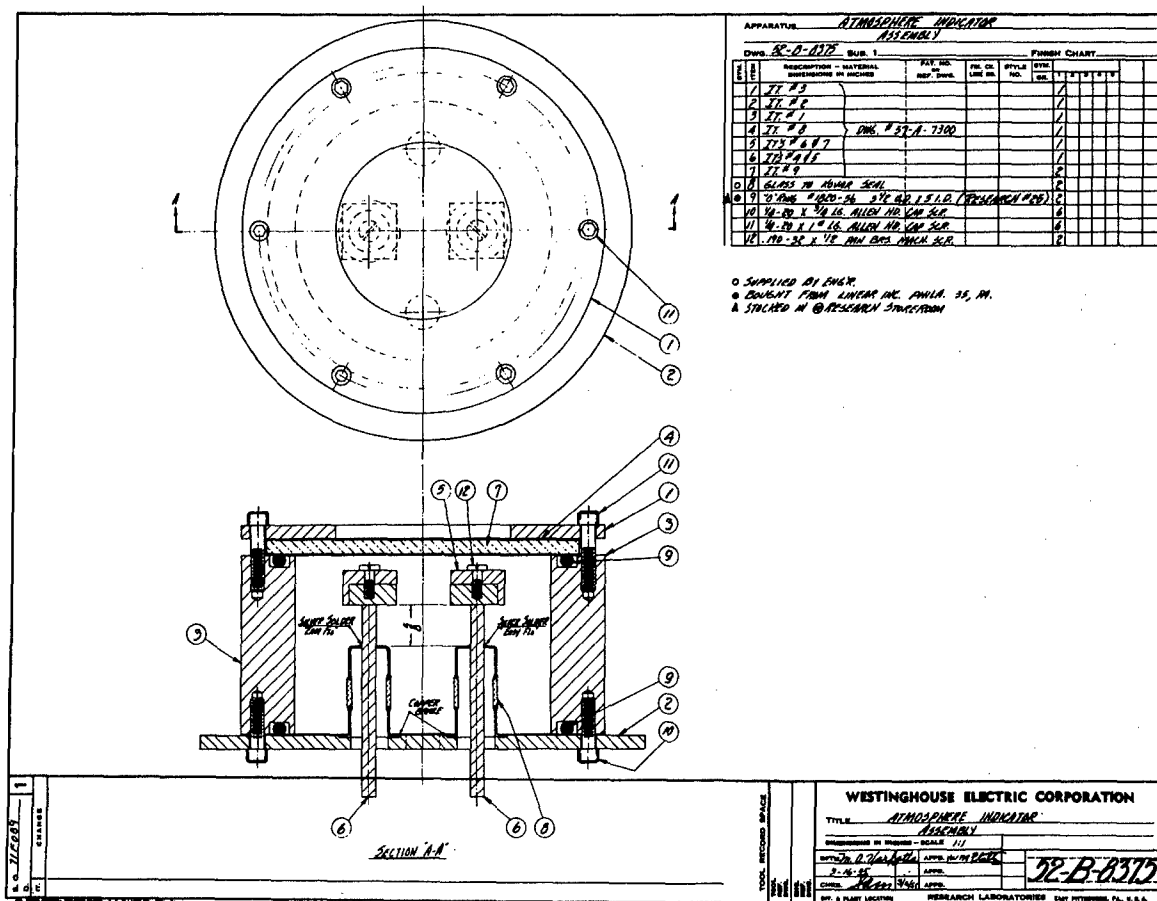


Fig. 7 - Atmosphere Indicator

easily adapted to determine the oxygen and nitrogen content of inert gases in amounts less than 0.02%. Earlier work has indicated that the maximum amount of oxygen that may be tolerated in welding atmospheres for molybdenum is smaller by at least an order of magnitude. It is apparent that a more sensitive means of impurity indication is required in these investigations. The concentration of oxygen in an atmosphere has been indicated to 10^{-25} mm partial pressure by Rathenau and de Wit.⁵ This device depends on the variation of the dissociation pressure of metal oxides as a function of the temperature. Lustman⁶ points out that in a given atmosphere a metal will not oxidize if the

dissociation pressure of the oxide is greater than the partial pressure of oxygen in the atmosphere. In the unit proposed by Rathenau and de Wit, the formation of the oxide is observed visually on heated strips of metal foil. Lustman⁶ has given the partial pressure of oxygen for oxide formation on a number of metals so that from observation of the metal surface it is possible to determine the partial pressure of oxygen in the atmosphere around the metal foil. Lustman's⁶ oxide data are shown in Fig. 6. A modified unit based on these principles of operation has been designed for use in conjunction with the gas purification system and welding chamber. The assembly drawing of this unit is shown in Fig. 7. Metal foil will be attached between the two conductors and heated electrically. The temperature will be controlled by optical pyrometric means.

The purity indicator has been constructed but has not yet been calibrated for use.

III WELDING ARC-CAST MOLYBDENUM

Studies reported earlier showed that the welding properties of properly deoxidized arc-cast molybdenum were superior to the sintered material. Hence, the major portion of the work on fusion welding was done using arc-cast material. The arc-cast lots of molybdenum used in the investigations described in this report were deoxidized with several different materials. The major portion of the work was done with carbon deoxidized molybdenum, but studies were also made using aluminum, titanium, and a combination of carbon and titanium. The experimental work on these materials was done under three different welding atmospheres: welding grade argon, purified argon and a selected grade of charcoal purified helium.

The analyses of the arc-cast material used in the welding tests conducted during the past year are shown with the analyses of material used in earlier work, Table I.^{1,2} The analyses of some of the materials used in the latter portion of this report period are not yet complete.

TABLE I
CHEMICAL ANALYSES OF ARC-CAST MOLYBDENUM

<u>Element</u>	<u>Lot #1</u> <u>(C Deox.)</u>	<u>Lot #2</u> <u>(Al Deox.)</u>	<u>Lot #3</u> <u>(C Deox.)</u>	<u>Lot #4</u> <u>(Ti Deox.)</u>	<u>Lot #5</u> <u>(Ti Deox.)</u>
Carbon	0.06	0.01	0.04	0.05	0.015
Oxygen	0.0018	-	0.002	0.001	-
Nitrogen	0.003	0.003	0.004	0.003	0.007
Aluminum	0.012	0.16	0.04	0.012	-
Iron	0.014	0.011	0.01	0.102	-
Nickel	0.003	0.011	0.003	0.005	-
Tungsten	-	0.04	0.02	nd	-
Arsenic	np*	0.0002	0.0002	nd	-
Manganese	0.001	0.002	0.002	0.001	-
Lead	0.005	0.005	0.005	0.005	-
Tin	-	nd	nd	nd	-
Silicon	0.005	0.005	0.005	0.005	-
Barium	0.01	nd	nd	0.01	-
Chromium	0.005	nd	nd	0.005	-
Copper	0.0002	nd	nd	0.0002	-
Magnesium	-	0.002	0.002	nd	-
Titanium	nd**	nd	nd	0.46	0.53

* NP - Not Present

** ND - Not Determined

The work reported in the first and second annual reports was conducted using the molybdenum from Lot #1 with a few tests on material from Lot #2. The material from Lots #2,3,4, and 5 was used in the weld tests which are discussed in this report.

A. Welding Atmosphere Tests

The welding test data have been grouped according to the type atmosphere used. This grouping is arbitrary and is used for convenience.

(1) Welds in High Purity Helium

Helium, having a purity believed to be better than that commercially available, was procured directly from the U.S. Bureau of Mines. This helium had been charcoal purified and was reported to be low in oxygen and nitrogen. Mass spectrometer analysis showed this gas to contain 0.01 to 0.02% O_2 and 0.04 to 0.09% N_2 , which is better than the welding grade argon and commercial helium with respect to oxygen and nitrogen. However, the impurity concentration still appears to be larger than that required for molybdenum welding applications. This helium was used as an atmosphere while welds were made in the 0.04% C, 0.06% C deoxidized and 0.16% Al deoxidized arc-cast molybdenum procured earlier. The chemical analyses of these materials are given in Table I.

Carbon deoxidized molybdenum was used to make three welds. The welding data are given in Table II. The welds in the carbon deoxidized molybdenum made under helium had a wider fused zone than welds made using argon as an atmosphere. The increase in fusion is due to the higher arc voltage required for helium atmospheres. Since the welding current was maintained at approximately the same value as had been used with argon, the energy input to the welding arc is larger and the amount of fused molybdenum in the weld bead is proportionately greater. The increase in the bead width was reflected in increased thermal distortion in the weld specimen. The stresses resulting from this internal shrinkage and distortion were sufficient to cause catastrophic cracking at the weld crater. This condition was found in all three welds made

TABLE II
WELDING DATA

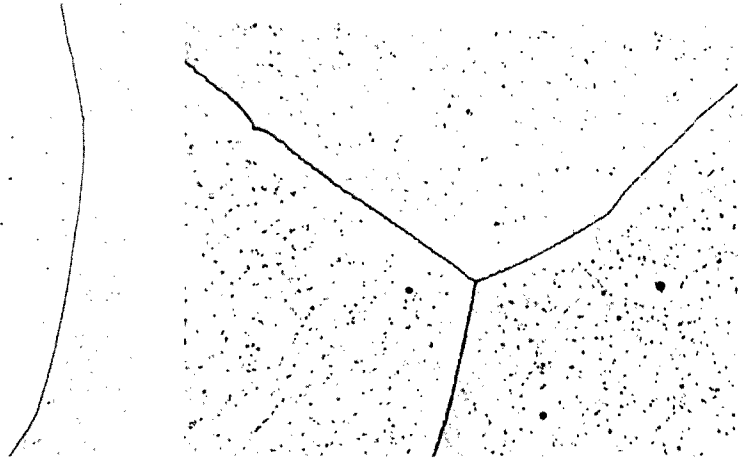
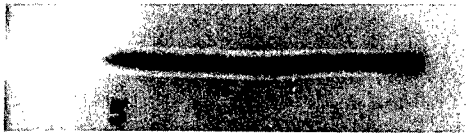
<u>Sample</u>	<u>O₂</u>	<u>N₂</u>	<u>H₂O</u>	<u>Bal.</u>	<u>Welding Current Amps.</u>	<u>Voltage</u>	<u>Arc Travel Speed In./Min.</u>	<u>Comments</u>
He 1*	Not Det.	<0.05	-	He**	Recorder Failure	15.5	6	Bright weld crater crack; wide bead, 100% penetration, blue haze on sur- face.
He 2	Not Det.	0.6	-	-	200	17.5	6	Wide bead; film on surface; no cracks; used hot Ti chips, 1500°F getter train.
He 3	Not Det.	0.6	-	-	200	17-21	6	Wide bead with crater crack. Distortion caused voltage shift. Hot Ti getter train used.
He 4	Nil	(N ₂ :H ₂ O 0.5)	0.5)	He**	175	-	6.1	Clean, bright, no cracks as welded; cracked explosively 2 to 20 hrs. later.
He 5	0.1	0.09	0.22	He	175	-	6.1	Same as He4 but cracked with slightly less violence after 1 to 1-1/2 hrs.
He 6	0.02	0.04	0.02	He	175	-	6.1	Same as He4; cracked when held too tightly. Evidence of consider- able thermal dis- tortion.
HeAl 1	0.02	0.05	0.01	He	170	-	6.1	Plate appears dirty from metal vapor; bead surface rough; chevron cracks in weld.
HeAl 2	0.01	0.07	0.02	He	170	-	6.1	Same as HeAl 1.

*This weld in 0.06% C material, remainder in 0.04% C material except those marked HeAl 1 and HeAl 2 which were in 0.16% aluminum deoxidized molybdenum.

**This gas was checked for hydrocarbons and found to contain less than .005%.

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Fig. 8 - Radiograph and Photograph
of a Weld in 0.04% C
Deoxidized Molybdenum
Made in Charcoal Purified
Helium, He5.



(a)
P55-108-3 He6
100X

(b)
P55-176-1 He7
300X

Fig. 9 - Weld in 0.04% C Deoxidized Mo Welded Under Charcoal Purified Helium.

in the carbon deoxidized molybdenum. The cracks in these welds occurred after the test plate had been removed from the welding chamber for 1 to 20 hours. The residual stresses apparently increased with decreasing temperature to a level above the fracture stress. The ductility, therefore, decreased to the point where brittle failure resulted and the specimens cracked with some violence. In one case the fractured portion was moved a distance of 18 inches from its original location. Catastrophic failure at the weld crater was encountered in other materials and welding

atmospheres and the residual stresses causing these failures will be discussed in a later section.

An examination of the helium shielded welds made in carbon deoxidized molybdenum, of which the weld in Fig. 8 is typical, shows that the welds are sound with the exception of crater cracks due to residual stresses. Photomicrographs of two typical welds are shown in Fig. 9. Metallographic examination of the weld zone showed a dispersion of carbides in the grains.

Two chemical analyses were made of the weld areas. In order to obtain samples of sufficient size to reduce the analysis error, it was necessary to use one weld sample for each analysis for O₂, N₂, and C. These analyses are compared to that of the unwelded plate in Table III. These data indicate that there is very little contamination of the fused metal in welds made in the charcoal purified helium atmospheres.

TABLE III
CHEMICAL ANALYSES OF WELDS IN ARC-CAST CARBON
DEOXIDIZED MOLYBDENUM MADE UNDER PURIFIED HELIUM

	Wt. %			Atomic %*		
	O	N	C	N + C	N	C
Weld He 4	-	-	0.03	.26	.02	.24
He 5	-	0.004	-	.26	.02	.24
He 6	0.01	-	-	.26	.02	.24
He 7	0.001	0.004	-	.26	.02	.24
He 2	-	0.012	0.04	.38	.06	.32
Plate	0.002	0.004	0.04	.34	.02	.32

*Where values of wt. % not available, assumed same value as weld made under similar conditions.

Bend test data were taken on samples He2 and He6. These data are shown in Table IV and Fig. 10. There is some doubt as to the existence

TABLE IV
BEND TEST DATA
WELDS He2 AND He6

0.04% CARBON DEOXIDIZED MOLYBDENUM
WELDED UNDER SELECTED PURITY HELIUM

Sample	Test Temp. °F	Thickness Inches	Width Inches	Load at Proportional Limit, Lbs	Max. Load Lbs	Load at Fracture Lbs	Bend Deflection Inches
He2	-160	.051	.251	-	-	62	-
	- 80	.051	.251	63	-	77.5	.019
	80	.051	.2505	42	55.8	47.8	.309
	160	.051	.251	27	-	41.5	.131
	240	.0505	.251	19	36	35.5	.213
	320	.051	.251	13	31.5	No Fracture	.500
He6	-320	.050	.245	-	-	87	-
	-240	.050	.245	73	-	91.5	.004
	-160	.050	.245	56	-	70.5	.002
	- 80	.050	.246	41	-	77	.049
	80	.050	.246	34	59.3	56	.207
	160	.050	.245	24	-	41.5	.174
	200	.050	.245	19	-	39.5	.143
	240	.050	.246	18	37.5	No Fracture	.500

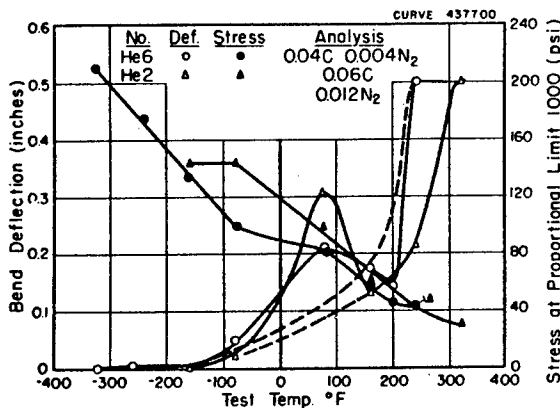


Fig. 10 - Welds Made in Arc-Cast Carbon Deoxidized Molybdenum Under Helium Atmosphere.

of the inflection points in the bend deflection curves for the welds in carbon deoxidized material made under helium atmospheres. For this reason, the dotted curves are also shown in the conventional shape. The data in Fig. 10 show that these welds were ductile (120° bend) at 240°F to 320°F. A comparison of

these data with those reported previously may be made by examination of Figs. 11 and 12 which are reproduced from earlier work.² The new points have been added. These points do not fit the curves based on previous

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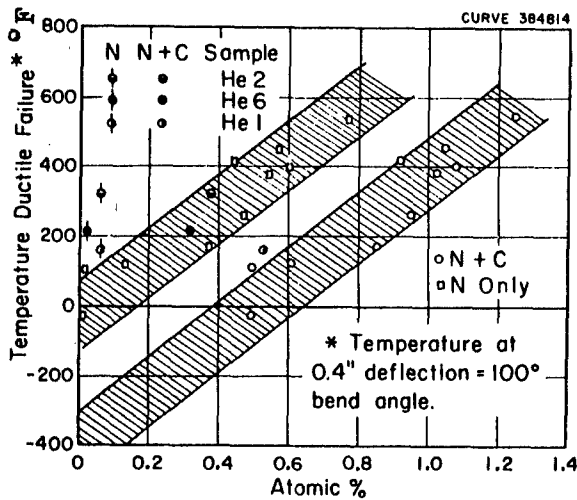


Fig. 11 - Relation Between Transition Temperature* and Atomic Per Cent Carbon and Nitrogen in Weld Bead

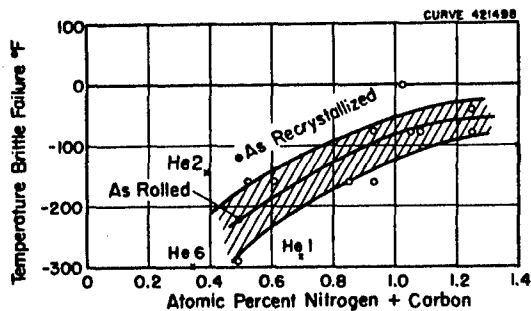


Fig. 12 - Effect of Nitrogen and Carbon in Molybdenum Weld Beads Upon the Temperature of Brittle Failure

as compared to 0.06% in sample He 1.

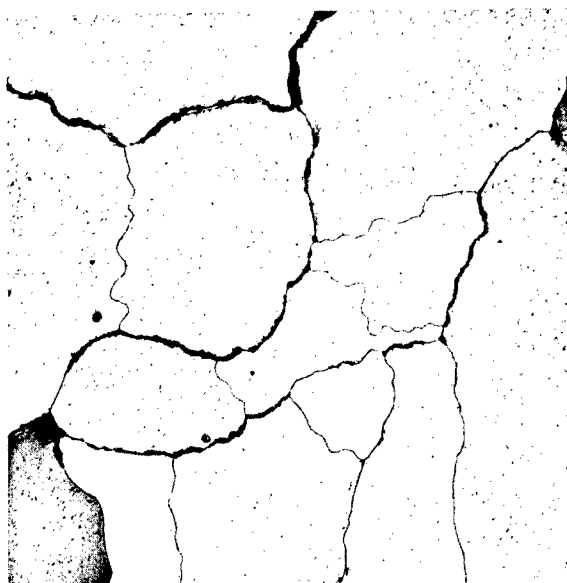
Aluminum deoxidized arc-cast molybdenum was welded under a charcoal purified helium atmosphere, Table II. A typical weld in this material is shown in Fig. 13. A large quantity of condensed metal vapor was found on the backup plate and on the weld sample. It is probable that this vapor was produced by the aluminum in the molybdenum since aluminum boils at temperatures below the melting point of molybdenum. The

data. The ductile failure points for He2 and He6 are considerably above their expected locations. An explanation for this difference will be discussed in detail in the section on argon atmospheres. Sample He 1, from earlier work, is close to the original scatter band in Fig. 11. The points for brittle failure correspond reasonably well with the values obtained earlier, Fig. 12.

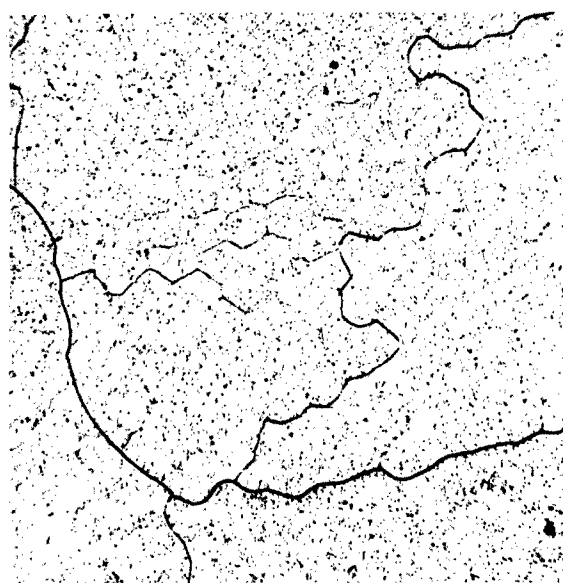
Welds He2-He7 all showed crater cracks, some of which were violent in nature, Table II. These welds were made from a different lot of carbon deoxidized molybdenum than weld He 1. The principal difference was that the carbon content of the material used for samples He2 to He7 contained 0.04% carbon



Fig. 13 - Radiograph and Photograph of a Weld in 0.16% Al, Arc-Cast Molybdenum Made in Charcoal Purified Helium HeAl 1.



(a) P55-108-4
100X



(b) P55-108-6
300X

Fig. 14 - Weld in 0.16% Al Arc-Cast Molybdenum Made Under Charcoal Purified Helium HeAl 1.

cracking in the welds occurred before the weld was removed from the chamber and the probability is good that these cracks were formed while the fused zone was very hot. This type cracking seems to be characteristic of aluminum deoxidized molybdenum welded under helium. The welds in this material made under helium all showed a similar type of cracking. However, a weld made earlier in this material under argon did not show chevron cracks.² Typical photomicrographs of welds made under helium

in aluminum deoxidized molybdenum are shown in Fig. 14. The cracks in this sample were intergranular in nature. The wide grain boundaries shown in Fig. 14(b) at 300X are characteristic of the aluminum deoxidized material. As shown in this photomicrograph, the boundary width is not always constant. It should also be noted that the boundary film seems to have penetrated the sub-boundaries. The boundary film was at first thought to be aluminum or aluminum oxides both of which have melting points below that of molybdenum. However, the wide grain boundary "films" were found to be due to an etching characteristic of the material which shows wide grain boundaries because of differences in the height of different grains.

(2) Welds Made Under Argon Atmospheres

Atmospheres of welding grade and repurified argon were used to determine the effect of atmosphere purity upon the ductility of the weld metal. Work reported in the second annual report on "Joining Molybdenum"² did not show the tendency toward catastrophic cracking encountered when helium atmospheres were used. However, two different lots of carbon deoxidized molybdenum were used in these tests as well as the welding atmosphere change from argon to helium. In order to re-establish a control on the experimental variables, a weld was made in Lot #3 molybdenum, Table I, under an atmosphere of welding grade argon. This weld was not subject to crater cracking observed in the samples of this material welded under helium. This placed the helium atmospheres under suspicion. However, welds made later using the 0.04% carbon material, Lot #3, under purified argon showed catastrophic cracking. This condition suggested that either the material was different in some manner or the atmosphere purity was too great. To check the latter point, several more welds were made in welding grade

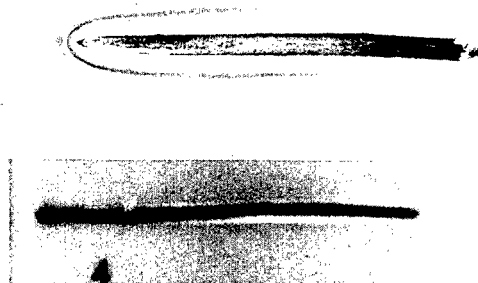
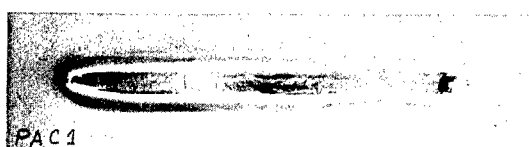


Fig. 15 - R-13935 - Radiograph and Photograph of a Weld in 0.04% C Deoxidized Molybdenum Made Under Welding Grade Argon



1 —



2 —

Fig. 16 - R-14167, R-14166 - Photographs and Radiographs of Typical Welds in 0.04% C Deoxidized Mo Made Under Purified Argon

argon. Some of these welds suffered catastrophic cracking, indicating that atmosphere purity was not responsible. Examination of the chemical analyses of the two lots of material showed only the difference in carbon content as a reason for the difference in properties. Studies made later indicated that the difficulty rested in the residual thermal welding stresses so that discussion of this phase of the investigation will be completed in detail in the section on residual stresses.

For comparison of properties and chemical analyses, two welds were made in the 0.04% carbon deoxidized material under welding grade argon. One of these welds is shown in Fig. 15. Seven welds were made in the same material under repurified argon and two typical welds are shown in Fig. 16. The welding data and description of the welds are given in

Table V.

Chemical analyses of the weld beads made under welding grade and purified argon indicate an improvement in the impurity content of the

TABLE V

WELDING DATA FOR WELDS MADE UNDER ARGON
ATMOSPHERES IN 0.04% CARBON DEOXIDIZED MOLYBDENUM

Weld	Atmosphere Analysis				Welding Current Amps	Welding Voltage	Arc Travel Speed "/Min	Comments
	N ₂ or CO	O ₂	H ₂ O	H				
A44	Welding grade argon No analysis				180	12	6.1	Bright weld. No cracks.
A46	Welding grade argon No analysis				175	14	6.0	Weld clean, uncracked. Cooled in chamber same as PAC2.
PAC1	<0.02	<0.02	<0.03	<0.04	180	15	6.0	Purged 30 cycles with welding grade argon. Purge continued at 1 cu ft/hr during heating period on furnace 4-5 hrs. This slow purge done through dry ice acetone trap, P ₂ O ₅ , and hot Zr (1000°C). Purged four times with purified argon. Gas recirculated through purifier 45 min before welding.
PAC2	0.02	0.02	0.03	0.02	180	15	6.0	Standard 30 cycle purge with welding grade argon. With Zr chips at 1000° purged 10 times through purifier 1-3 cu ft/hr. Recirculated 40 min through purifier. Weld cooled in chamber; crater crack to edge of plate.

TABLE V
(CONTINUED)
WELDING DATA FOR WELDS MADE UNDER ARGON
ATMOSPHERES IN 0.04% CARBON DEOXIDIZED MOLYBDENUM

<u>Weld</u>	<u>Atmosphere Analysis</u>				<u>Welding Current Amps</u>	<u>Welding Voltage</u>	<u>Arc Travel Speed "/Min</u>	<u>Comments</u>
	<u>N₂ or CO</u>	<u>O₂</u>	<u>H₂O</u>	<u>H</u>				
PAC3	0.06 \pm .02	<0.02	<0.1*	0.05 \pm 0.02	180	15	6.0	Purge same as PAC2. Weld has small crater crack.
PAC4	0.06 \pm .02	0.02	0.1*	0.05 \pm 0.02	175	15	6.0	Purge same as PAC2, weld left in chamber 2 min cracked audibly; entire crater end came off, moved 1/16" under hold-down plate.
PAC5	0.03 \pm 0.02	<0.02	<0.1*	0.05 \pm 0.02	175	15	6.0	Purge same as PAC2. Very clean bead, crater crack.
PAC6	0.03 \pm 0.02	<0.02	<0.1*	0.05 \pm 0.02	175	14.8	6.0	Purge same as PAC2. Clean bead; crater crack; arc flutter last half of bead.
PAC7	Data not available				178	14.7	6.0	Purge same as PAC2; clean bead; crater crack occurred when placed on table very carefully. Crater end flew 8".

*Limit of detectability due to background conditions.

material. These data are given in Table VI. The data indicate that with respect to oxygen and nitrogen, the weld beads made under purified argon compare favorably with the analysis of the unwelded plate. Results reported earlier^{1,2} indicate that welds made in welding grade argon will contain 0.004% oxygen in the weld bead. These data indicate that improvement of the weld metal by further purification of the welding atmosphere may not be too successful. It has also been observed that samples welded under welding grade and purified argon were both subject to cracking at the weld crater, and that the oxygen below 0.02% and nitrogen below 0.05% seem to have little effect on the tendency to crack.

TABLE VI
NITROGEN AND OXYGEN CONTENTS OF
WELDS MADE IN ARGON ATMOSPHERES

<u>Sample</u>	<u>Atmosphere</u>	<u>Weld Bead Analysis</u>	
		<u>N₂</u>	<u>O₂</u>
Al4	Welding Grade Argon	0.016%	-
PAC1	Purified Argon	0.008	-
PAC2	" "	0.005	-
PAC7	" "	-	0.003%
Unwelded Plate	-	0.004	0.002%

Physical test data for welds made under welding grade and under purified argon in the 0.04% C material are given in Table VII. These data are presented as curves in Fig. 17. The curves in Fig. 17 indicate that the use of purified argon and the reduction of nitrogen and oxygen in the weld metal, Table VII, decreased the ductility of the material. These data are in contradiction with data collected earlier which indicated that decreasing the nitrogen should improve the ductility

TABLE VII
TEST DATA FOR WELDS MADE IN 0.04% C DEOXIDIZED MOLYBDENUM
WELDED UNDER ARGON

Sample	Test Temp. °F	Deflection Rate "/Hr	Deflection Inches	Stress at Proportional Limit, PSI
A44	320	6	.500*	38,000
	240	6	.273	46,200
	160	6	.194	63,400
	80	6	.178	81,500
	- 80	6	.007	137,500
	-160	6	.003	144,800
	-240	6	-	166,500
PAC4	400	6	.500*	32,200
	320	6	.297	39,300
	80	6	.067	116,000
	- 80	6	.008	221,500
	-160	6	.006	203,500

*Maximum deflection - no fracture.

at low temperatures.² A possible explanation for this contradiction would be the scatter expected in data from bend tests. Some of the earlier work² indicated that with the same material and atmosphere, scatter up to $\pm 50^{\circ}\text{F}$ could be expected in bend test results. If the purified atmosphere accomplished only slight improvement and the bend

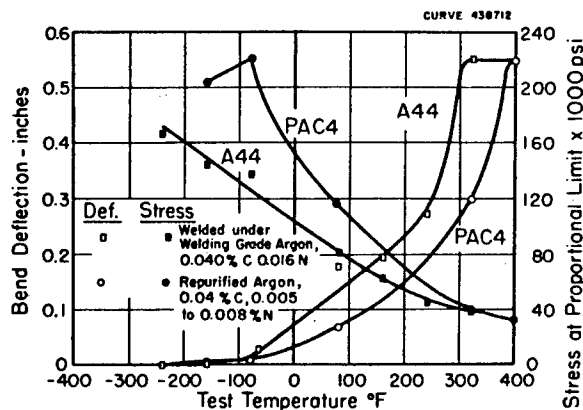


Fig. 17 - Welds in Arc-Cast 0.04% Carbon Deoxidized Molybdenum. Argon Atmosphere. Welds PAC4 and A44.

deflection curve obtained for the weld made in welding grade argon was fortuitously low, the bend deflection curves shown in Fig. 17 could occur.

The bend test data in Fig. 17 show the temperature for maximum deflection to be 300 to 400°F for the welding grade and purified argon respectively. These values are 100 to 200° higher than

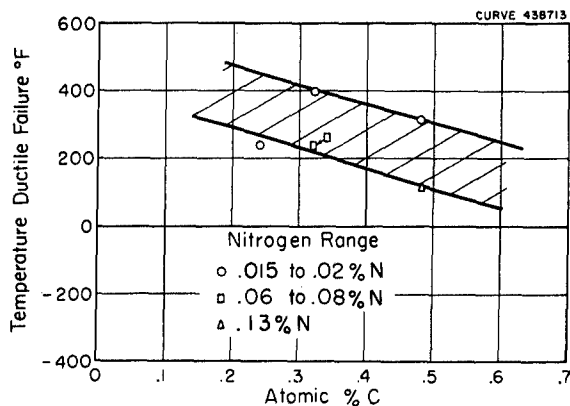


Fig. 18 - Temperature for Ductile Failure vs. Carbon Content

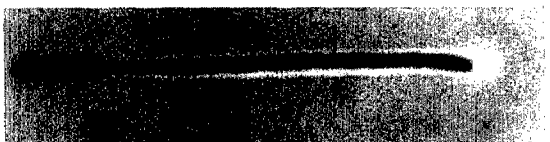
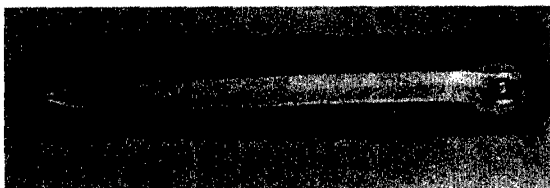


Fig. 19 - R-13934 - Photograph and Radiograph of a Weld in Aluminum Deoxidized Arc-Cast Molybdenum Made Under Argon Atmosphere

Examination of the chemical analyses given in Table I shows little difference in these materials with the exception of the carbon content. There is a difference in Ba, Cu and Cr, but these are believed to be minor in effect as compared to the carbon. Using welds in both the material from Lot #1 and Lot #2, a qualitative estimate of the effect of carbon may be obtained. The data are inadequate for firm conclusions but do indicate the possible effect of carbon, Fig. 18. It was originally thought on the basis

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the values obtained earlier for similar nitrogen contents in the weld metal. The points in Fig. 11 which fall within the scatter band were collected using 0.06% carbon deoxidized molybdenum, Lot #1, Table I. The points outside the scatter band for welds He2 and He6 were obtained using 0.04% C deoxidized molybdenum, Lot #3, Table I. The same material was used for the welds Al44 and PAC4, Table VII, and the nitrogen analyses in Table VI indicate that for weld Al44 and welds similar to weld PAC4, the points for the maximum deflection temperature as a function of the nitrogen content will fall outside the scatter band in Fig. 11.

of the interstitial effectiveness of carbon and nitrogen that they would have similar effects in reducing the ductility at low temperatures, Fig. 11.² However, qualitatively, it appears from Fig. 18 that as the carbon is increased the ductility at lower temperatures is improved. It seems probable that the effect of carbon in excess of the solid solubility limit⁷ is that of deoxidization rather than that of an alloy addition. If this is the case, and the data in Fig. 18 are properly interpreted, the range of carbon contents between 0.06 and 0.1% should be investigated.

In the case of carbon deoxidized molybdenum, it is apparent that the effect of carbon content may be able to counteract the effects of welding in a high purity atmosphere. The work with purified argon atmospheres and carbon deoxidized arc-cast molybdenum indicates that further changes or improvement in the welding atmosphere will lead to little improvement in the ductility obtained in the weld metal. However, there seems to be an indication that changes in the material composition may be a fruitful field of investigation.

Aluminum deoxidized arc-cast molybdenum was welded in welding grade argon and in purified argon to determine the effects of these atmospheres on the properties of the welds. Work described earlier showed that aluminum deoxidized arc-cast material was subject to hot cracking when welded in commercial and charcoal purified helium. However, this material had been satisfactorily welded under atmospheres of welding grade argon.² This anomaly obviously needed further study. In order to recheck the previous results, a weld was made in welding grade argon and is shown in Fig. 19. This weld showed no cracks after welding. Welding data for welds made in aluminum deoxidized molybdenum are given in Table VIII. Included in this table are data for welds made previously under argon atmospheres.

Physical test data were obtained for two welds made under welding grade argon. These data are given in Table IX, and are presented in

TABLE VIII
WELDING DATA FOR WELDS
MADE UNDER ARGON ATMOSPHERES
IN ALUMINUM DEOXIDIZED MOLYBDENUM

<u>Sample</u>	<u>Atmosphere Analysis</u>				<u>Arc Current Amps</u>	<u>Nominal Arc Voltage</u>	<u>Arc Travel Speed In./Min.</u>	<u>Comments</u>
	<u>O₂</u>	<u>N₂</u>	<u>H₂O</u>	<u>H₂</u>				
Al 2	<0.02	0.6	-	-	180	14	6.0	Crater crack, blackened parent metal around bead.
AlA 45	<0.02	0.04	0.13	0.08	185	14	6.1	Slight haze on bead; rough surface; no cracks.
PAA1 1	<0.02	.02 ± .01	<0.03	<0.02	180	15	6.0	Purged 30 times with welding grade argon, 10 times with purified argon recirculated 30 min through purifier. Blackened area near bead on surface of plate. Typical of Al deoxidized material.
PAA1 2	<0.02	.18 ± .03	0.5	.05 ± .02	177	14.5	6.0	Purge same as PAA1-1. Bead clean. Plate discolored. No crack.
PAA1 3	<0.02	1.13 ± .08	0.1	.03 ± .02	177	14.7	6.0	Purge same as PAA1-1. Bead same as PAA1-2.

TABLE VIII
WELDING DATA FOR WELDS
MADE UNDER ARGON ATMOSPHERES
IN ALUMINUM DEOXIDIZED MOLYBDENUM

(CONTINUED)

<u>Sample</u>	<u>Atmosphere Analysis</u>				<u>Arc Current Amps</u>	<u>Nominal Arc Voltage</u>	<u>Arc Travel Speed In./Min</u>	<u>Comments</u>
	<u>O₂</u>	<u>N₂</u>	<u>H₂O</u>	<u>H₂</u>				
PAA1 4	<0.02	.13 \pm .03	0.1	.06 \pm .02	175	14.9	6.0	Purge same as PAA1-1. Bead clean, plate dirty, no cracks.
PAA1 5	<0.02	.08 \pm .03	0.5	.05 \pm .02	175	14.9	6.0	Purge same as PAA1-1. Bead same as PAA1-2. No cracks.
PAA1 6	-	-	-	-	177	14.3	6.0	Purge same as PAA1-1. Sample rejected. Mica insulation fell on bead during welding.
PAA1 7	-	-	-	-	177	15	6.0	Purge same as PAA1-1. Bead clean surrounded by blackened areas. No cracks.
PAA1 8	<0.02	.03 \pm .02	0.03	.05 \pm .02	175	14.9	6.0	Same as PAA1-7.
PAA1 9	-	-	-	-	175	15	6.0	Same as PAA1-7.

TABLE IX

**BEND TEST DATA FOR WELDS IN ALUMINUM DEOXIDIZED
ARC-CAST MOLYBDENUM MADE UNDER WELDING GRADE ARGON**

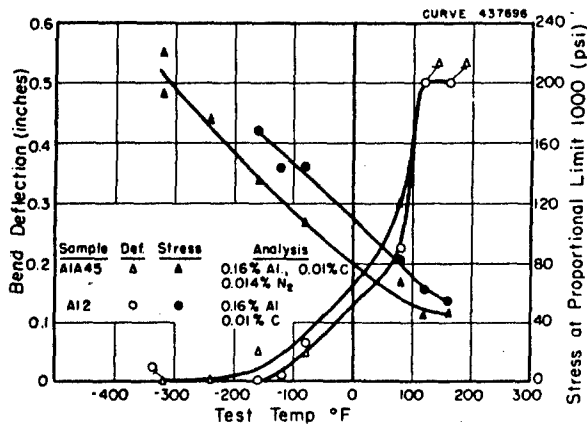
Sample	Test Temp. °F	Deflection Rate	Deflection Inches	Stress at Proportional Limit PSI
Al 2	160	6"/hr	.500*	46,300
	120	6	.500*	45,000
	80	6	.299	67,500
	- 80	6	.049	107,500
	-160	6	.051	135,000
	-240	6	.001	175,000
	-320	6	.001	220,000
	-320	6	.000	191,000
AlA 45	160	6"/hr	.500*	54,300
	120	6	.500*	62,500
	80	6	.226	81,500
	- 80	6	.065	144,000
	-120	6	.010	142,000
	-160	6	-	168,500

*Maximum deflection - no fracture.

the form of curves in Fig. 20. These welds were ductile (able to withstand 120° bend) at 120°F. The samples were completely brittle at -160 to -300°F. These results are among the best obtained for welds in

molybdenum.

A metallographic examination of the welds made in aluminum deoxidized molybdenum offers some explanation for the improved bend ductility found in these samples. Figs. 21 and 22 show a typical weld area. The grain size of these samples is large but is much smaller than was observed in samples of carbon deoxidized molybdenum.

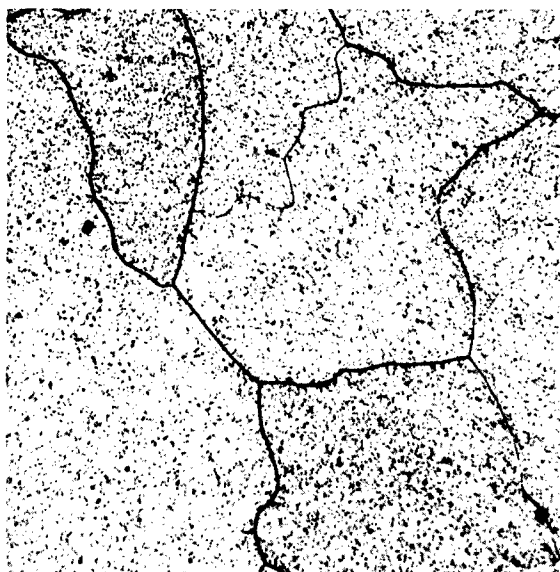


**Fig. 20 - Welds in Arc-Cast Aluminum Deoxidized Molybdenum.
Made under argon atmosphere.**



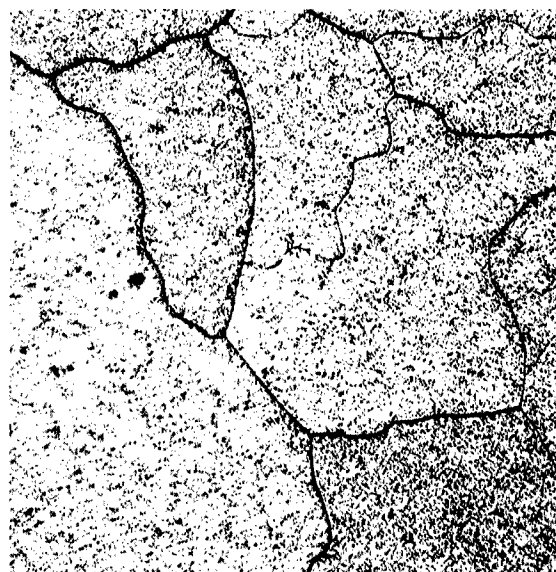
P54-144-1

Fig. 21 - Weld Zone in Aluminum Deoxidized Arc-Cast Molybdenum, Al-2, 100X.



P55-176-6

(a) Direct Illumination
300X



P55-176-5

(b) Oblique Illumination
300X

Fig. 22 - Weld Zone in Al Deoxidized Arc-Cast Molybdenum. Sample ALA 45.

There is also a marked substructure which may give the material fine grain characteristics. This grain size effect would reduce the effectiveness of deleterious grain boundary films caused by oxygen or nitrogen. Hence, the ductility of the welds would be improved over a carbon deoxidized material of similar degree of oxygen and nitrogen contamination. It was first thought that the wide grain boundaries observed in the aluminum deoxidized material were due to films of aluminum oxide or an aluminum oxygen molybdenum alloy. However, examination under oblique illumination showed that the boundaries were due to differences in etching rates in the electro-polished samples. Apparently the differences in grain orientation and the rates of solution are such that the boundary exists as a sloping step and under direct illumination this step appears as a wide grain boundary. Thus the aluminum deoxidized material seems to be better than some of the work with helium atmospheres indicated. The metallographic examination also indicates that the grain growth in the area adjacent to the weld was restrained during welding. Reduction in the grain growth permits a larger number of nuclei along the liquid-solid interface and will in turn cause a reduction in the grain size of the weld zone. This suggests that inhibiting the grain growth of the parent plate may decrease the grain size of the weld and improve its properties by means of a grain size effect.

Welds were made in purified argon using the arc-cast aluminum deoxidized material. Since chemical analysis, bend tests and possibly diffusion tests were to be performed on these samples, nine samples were made under the same welding conditions. These welds and their welding data were given in Table VIII. In the as-welded condition they were all free of cracks immediately after the samples were removed from the welding chamber and cooled to room temperature. However, after the samples stood for a few days cracks appeared. This is evidenced by the development of cracks between the welding of the sample

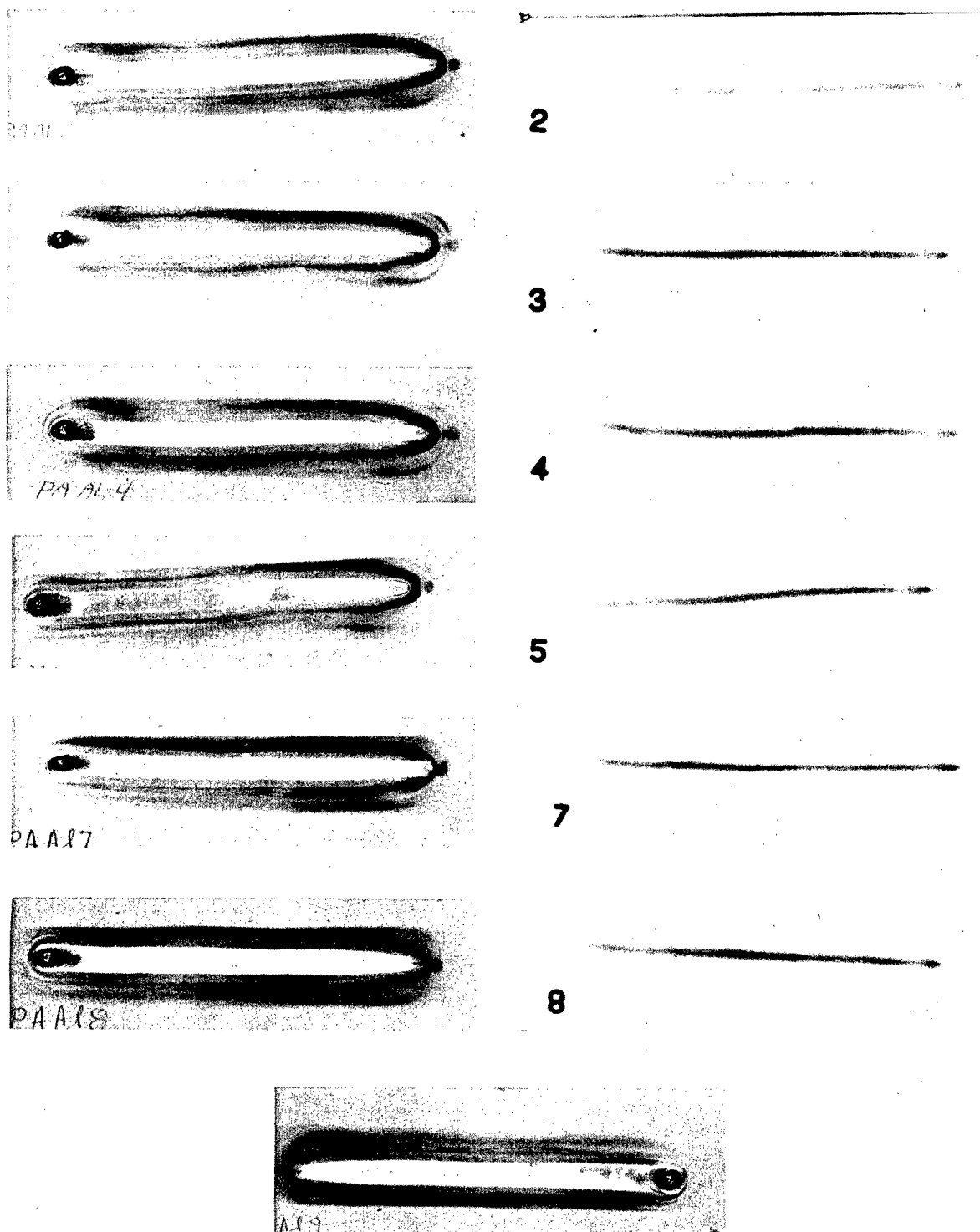


Fig. 23 - Photographs and Radiographs of Welds Made in Arc-Cast Aluminum Deoxidized Molybdenum Under Purified Argon.

and photographing and between leaving the photographic section and the time at which X-ray pictures were taken, Fig. 23. Some of the cracks developed after X-ray pictures had been taken. About 50% of the welded samples cracked over a period of approximately one week. The very nature of the weld test plate would leave large residual stresses in the plate which could cause cracking if the material were not sufficiently ductile. It was thought that this loss in ductility could be due to impurity pickup during welding. The nitrogen analysis for weld PAA1-1 was found to be 0.014% N. This nitrogen content is not high for welds in argon but seems to be high for welds in purified argon. The nitrogen content of the plate was found to be 0.003%. Analyses of the welding atmosphere indicated that the nitrogen in the atmospheres had increased. It seems probable that the Zr in the purifier had become exhausted when these tests were made.

A weld was made using argon purified after the Zr chips in the purification chamber had been renewed. This weld was sectioned and bend deflection tests made. The data for the bend deflection tests are given in Table X. These data are also shown in Fig. 24. The welds

TABLE X
BEND DEFLECTION DATA FOR WELD MADE IN ALUMINUM DEOXIDIZED
ARC-CAST MOLYBDENUM UNDER PURIFIED ARGON

<u>Test Temp.</u> <u>°F</u>	<u>Deflection</u> <u>Rate</u> <u>In./Hr</u>	<u>Stress at</u> <u>Proportional</u> <u>Limit, PSI</u>	<u>Deflection</u> <u>Inches</u>
160	6	48,200	0.500*
140	6	48,800	0.500*
120	6	53,000	0.226
80	6	89,400	0.144
0	6	124,000	0.108
-160	6	179,000	0.026
-200	6	222,000	0.002
-240	6	244,000	0.001

*Maximum deflection - no fracture.

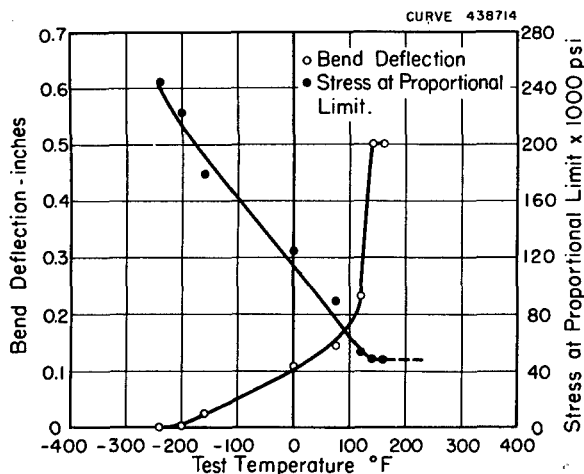
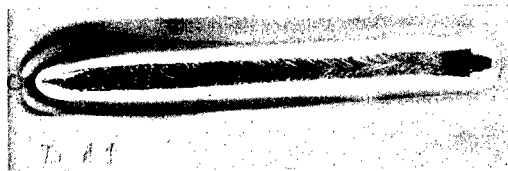


Fig. 24 - Weld in Aluminum Deoxidized Arc-Cast Molybdenum Made under Purified Argon. (PAAL 3)



1

Fig. 25 - Photograph and Radiograph of a Weld in Ti Deoxidized Arc-Cast Molybdenum.

dizer used was greater than the improvement, if any, due to the use of purified argon.

Arc-cast titanium deoxidized molybdenum was also used to make welds using welding grade and purified argon. Two lots of this material were used, Lots #4 and #5, Table I. Both of these materials are in the 0.5% Ti class, the principal difference being the difference in the carbon content. Lot #4 shows 0.05% C while Lot #5 contains 0.015% C. The complete chemical analysis of Lot #5 is not yet available. However,

were completely ductile in the bend test at 140°F and were completely brittle at -240°F. This weld did not show improvement in properties over the weld made under welding grade argon. However, since there was only 20°F difference in the temperature of completely ductile behavior, the results may fall within the expected scatter band for bend test data. However, since both the carbon deoxidized and the aluminum deoxidized molybdenum showed an increase in the temperature for completely ductile behavior, some question exists as to the improvement obtained by the use of purified argon. Comparison of the data obtained with aluminum and carbon deoxidized material shows that the improvement due to changes in the deoxi-

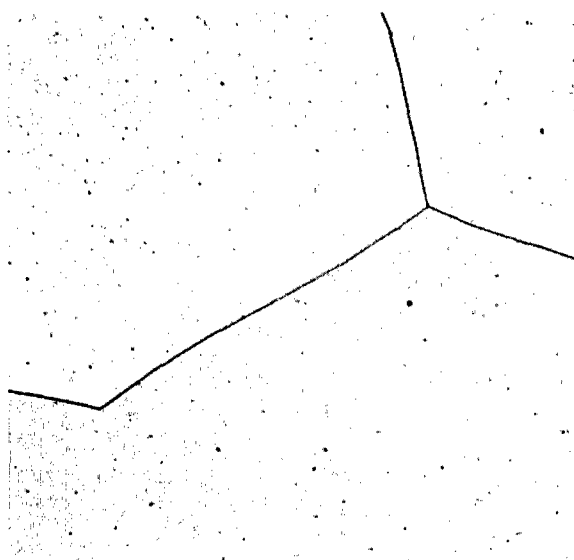


Fig. 26 - Weld Zone in Ti Deoxidized Arc-Cast Molybdenum. 100X

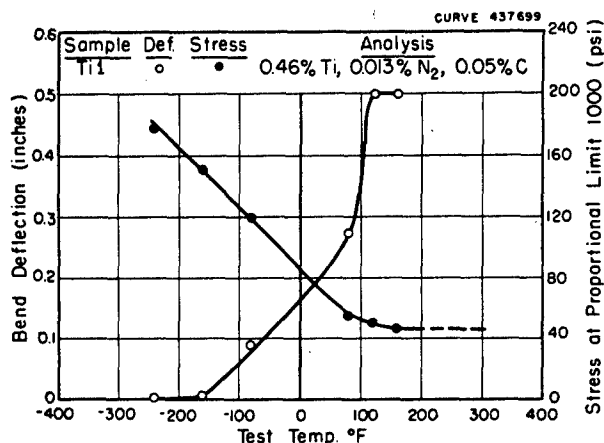


Fig. 27 - Weld in Arc-Cast Titanium Deoxidized Molybdenum. Made Under Argon Atmosphere.

The weld made under welding grade argon in Lot #4, titanium deoxidized arc-cast molybdenum containing 0.05% carbon, was made into bend test specimens and the results of the bend tests are given in Table XI. These data have been presented as curves in Fig. 27. The weld in this material was ductile (120° bend angle) at 120°F. The weld also shows

the spectrographic analysis does not show any qualitative difference.

Weld tests were made in the 0.46% titanium 0.05% carbon material from Lot #4. This material contains 0.003% nitrogen and 0.001% oxygen. Welds were made using welding grade argon and purified argon. The weld made under welding grade argon is shown in Fig. 25. A photomicrograph of the weld zone in this weld is shown in Fig. 26. This sample does not show the irregular grain boundaries observed in the titanium deoxidized vacuum sintered material or the arc-cast aluminum deoxidized molybdenum. The wide grain boundaries in Fig. 26 were examined under oblique illumination and it was found that the boundaries were due to differences in grain height and orientation.

TABLE XI
BEND TEST DATA - WELDS IN TITANIUM DEOXIDIZED ARC-CAST MOLYBDENUM
MADE UNDER ARGON ATMOSPHERES

<u>Sample</u>	<u>Test Temp. °F</u>	<u>Deflection Rate In./Hr</u>	<u>Stress at Proportional Limit, PSI</u>	<u>Bend Deflection Inches</u>
Ti A 1 (Welding Grade Argon)	160	6	46,500	0.500*
	120	6	51,000	0.500*
	80	6	55,400	0.272
	-160	6	120,000	0.087
	-240	6	177,000	0.001
Ti 4 (Purified Argon)	120	6	74,400	0.500*
	80	6	102,000	0.500*
	80	6	99,200	0.255
	0	6	149,000	0.059
	- 80	6	167,000	0.072
	-240	6	238,000	0.001
	-260	6	285,000	0.0008

*Maximum deflection - no fracture.

approximately 50° to 60° bend angle at room temperatures and 15° to 20° bend angle at -80°F. Examination of the curves in Fig. 27 shows that the material is ductile at the point where the stress at the proportional limit begins to rise. For this material the rise in stress occurs at a lower temperature than has been found for the carbon deoxidized arc-cast material used in earlier experimental work. The difference may be seen if the curves in Figs. 17 and 27 are compared. Both these welds were made in the same atmosphere and the principal known difference is the addition of 0.46% titanium to the molybdenum. The principal contaminating elements are very nearly the same for these two materials, Table I. It appears that the titanium addition makes an important contribution to the improved ductility of the welds.

A weld was also made using purified argon and the 0.46% titanium 0.05% C material from Lot #4. The bend test data are given in Table XI.

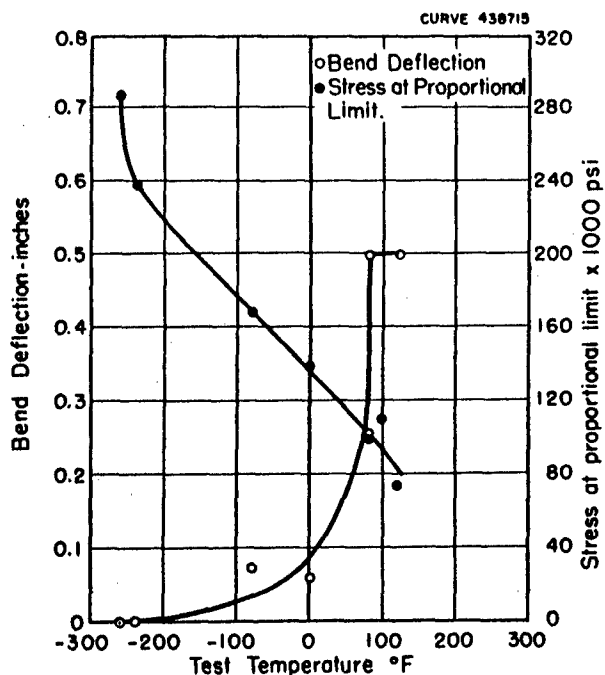


Fig. 28 - Weld in 0.5% Ti Deoxidized Arc-Cast Molybdenum (Lot #4) Made Under Purified Argon

(120° bend angle), however, in the case of the weld made under purified argon, this stable strength region of the curve was not reached. The value of the stress at the temperature of brittle behavior (0° bend) was found to be 285,000 psi. This value was much higher than that found in the same material welded under welding grade argon and higher than the maximum value attained in any other material examined previously. A possible explanation of these results may be found in the thickness of the bend test specimens used. The samples used in the weld made under purified argon were ground to 0.044 inch while other specimens were between 0.052 to 0.060 inch in thickness. It is possible that with this thickness difference the bending formula falls in a region in which the calculated stress at the proportional limit becomes more sensitive to the thickness. It is possible on the other hand that the stress values do apply and that the difference is in the material. In either case the bend deflection results on the 0.46% titanium from Lot #4 show the best results attained to date.

These data are shown as curves in Fig. 28. This weld showed the best bend ductility obtained to date. The weld metal was ductile; 120° bend at 80°F. The material was completely brittle in this test at -260°F. The stress at proportional limit curve, however, does not have the same appearance as the curve shown for the same material welded under welding grade argon, Fig. 27. Usually the stress at the proportional limit vs. temperature curve reaches a stable value at the temperature of ductile behavior

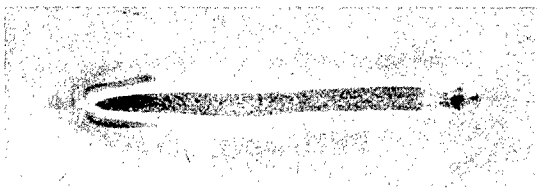


Fig. 29 - Weld in 0.53% Ti Deoxidized Molybdenum Containing 0.015% C, Atmosphere Purified Argon, Sample Ti 6

Several welds were made in the molybdenum containing 0.53% Ti and 0.015% carbon (Lot #5) using a welding atmosphere of purified argon. These welds were made using 180 amperes and 14 volts with an arc travel speed of 6.1 in. per minute.

Considerable difficulty was experienced in obtaining a weld which had not suffered large amounts of thermal distortion. The samples were distorted in such a manner that bend specimens could not be prepared without grinding the samples to half or one-fourth of their original thickness. A typical weld in this material is shown in Fig. 29. It should be noted that the weld samples in this material showed a reduced tendency to form crater cracks as compared to the welds in the carbon and aluminum deoxidized material. However, the only sample which was sufficiently flat to be used for bend test specimens was the only one which had stress relieved itself by the formation of a crater crack. The bend test data taken from weld Ti 9 are given in Table XII and these data are shown as bend deflection and stress at the proportional limit

TABLE XII
BEND TEST DATA
WELD UNDER PURIFIED ARGON ATMOSPHERE
IN 0.5% TITANIUM 0.015% C DEOXIDIZED MOLYBDENUM

Test Temp. °F	Deflection Rate In./Hr	Stress at Proportional Limit, PSI	Bend Deflection Inches
-240	6	275,000	.002
80	6	112,500	.212
160	6	57,500	.347
200	6	52,500	.500*

*Maximum bend deflection (120°).

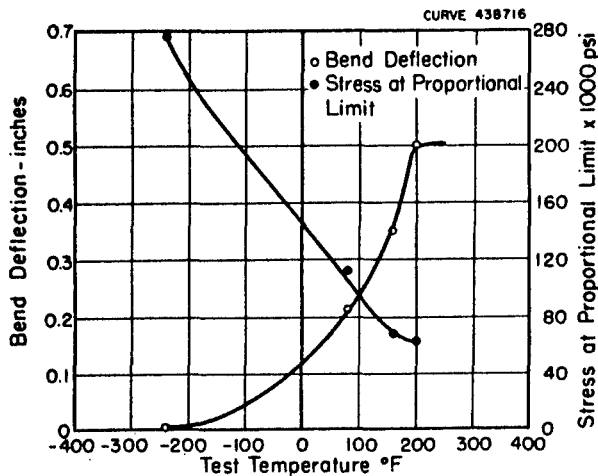


Fig. 30 - Weld in 0.53% Titanium, 0.015% C Deoxidized Molybdenum; Made Under Purified Argon, Tl 9

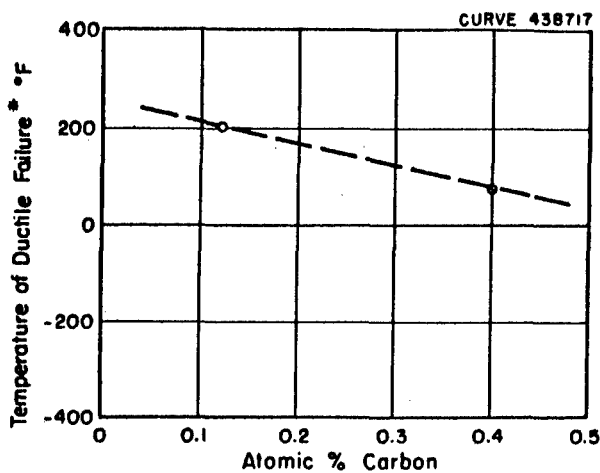


Fig. 31 - Temperature of Ductile Failure* vs Carbon Content in 0.5% Ti Deoxidized Arc-Cast Molybdenum. *0.5" Deflection or 120° Bend

some optimum value for the carbon content of the molybdenum weld metal and that this value is also effected by the presence of other alloying or deoxidizing elements in the material. The data shown in Figs. 18 and 31 are insufficient to establish firm conclusions; however, they appear to indicate a trend. More data are required on material with carbon contents in excess of 0.06% carbon and with additions of elements which improve the ductility of the weld metal.

curves in Fig. 30. Examination of these data shows that the temperature for ductile behavior was 200°F and the temperature for brittle behavior was near -260°F. These results were higher than expected for the low carbon material. A qualitative comparison between this material and the 0.05% carbon material containing 0.46% Ti shows the effect of carbon on the ductile behavior temperature as a function of the carbon content, Fig. 31. These data, along with those in Fig. 18, suggest that the original thinking on the effects of carbon was in error. In an earlier report², it was suggested that carbon and nitrogen might have similar effects on the ductility of molybdenum weld metal, Fig. 11. However, the data in Figs. 18 and 31 now indicate that the reverse condition is true. It seems probable that there is

If the data obtained on the effects of carbon are compared to the data obtained for nitrogen additions to the molybdenum weld metal, the difference in the slope of the curves for nitrogen and carbon would, if these materials are added in combination, produce a curve with a minimum. It seems apparent from the data shown for nitrogen and carbon, Fig. 18, that this condition has occurred in the case of the points which fall outside the scatter band. These points were for different concentrations of carbon at relatively constant nitrogen. Comparison of Fig. 18 and Fig. 31 shows that for a given carbon concentration the addition of Ti will lower the temperature of ductile behavior. It is apparent that the effects of Ti additions were additive. However, it is possible that further additions of Ti at constant carbon content may show a range where the effect of titanium either overcomes or is overcome by the effects of carbon. The need of more data on the effect of minor alloy addition on the ductility of molybdenum weld metal is apparent, and the data collected indicate that future work should be directed toward development of improved molybdenum alloys based on the properties of the weld metal without forgetting the requirements of the base metal.

B. Weld Crater Cracking

Weld crater cracks were observed during the entire welding program in both arc-cast carbon deoxidized and in aluminum deoxidized materials. Cracking occurred through and near the weld crater after the welds had cooled to ambient or near ambient temperatures. The cracks developed over a period of a few minutes to several weeks. In some materials the cracking occurred with violence. Since excessive amounts of crater cracks had not been observed in Lot #1, 0.06% carbon deoxidized molybdenum, the possibility of some difference in the material composition was sought. Check analyses were made of all three lots of material. The final results of these analyses are shown in Table I. In the case of tin and magnesium, Lot #1, the amounts indicated by the spectrographic analysis were so

small that the expense of developing techniques for wet chemical determination was not believed to be justifiable. A comparison of Lots #1 and #3 shows very little difference in the chemical analyses for elements known to be present, with the exception of Ba, Cu and Cr. It seems improbable that 0.01% barium would change the crater cracking characteristics of the material. However, it is possible that the barium acted as a deoxidizer since one of the oxides of barium melts at 1923°C and the estimated boiling point is near 2000°C. The low value of the boiling point would indicate a tendency toward porosity in the weld metal. However, this was not observed. The oxide may have a higher boiling point or the amount present may be too small to cause an observable change. It is believed that the barium had little, if any, effect on the tendency toward weld cracking. The small amounts of chromium and copper would not seem to account for any difference in properties. However, these elements might have a small effect on the ambient temperature strength of the material. The carbon content difference between Lot #1 and #3 seems to be the principal one. The effect of carbon on these materials was given earlier.

Occasionally, a weld made in the 0.04% C deoxidized arc-cast material, Lot #3, was found which had not suffered a crater crack. One

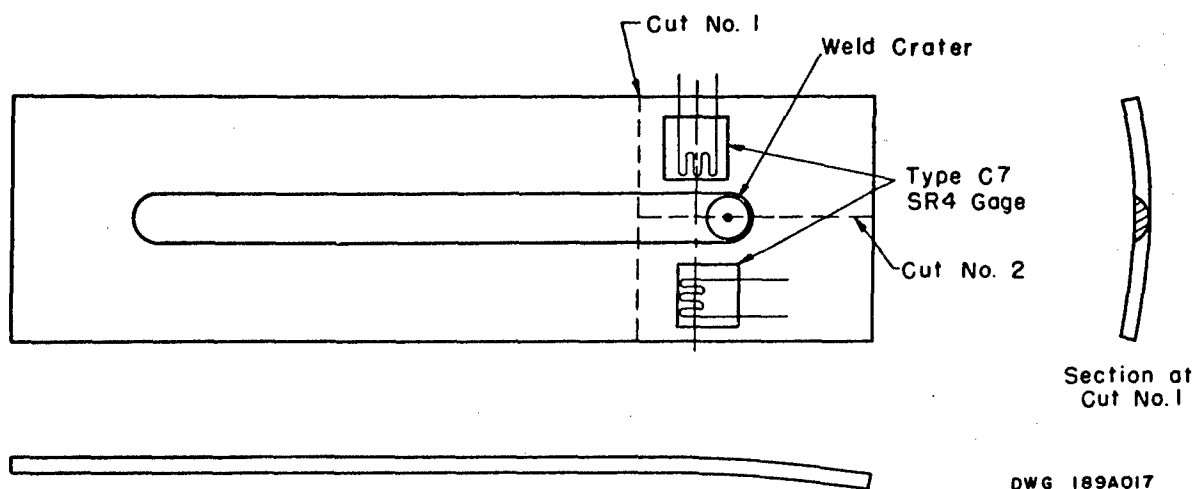


Fig. 32 - Weld Used for Strain Measurements

such sample was obtained after having been welded in purified argon. This sample showed evidence of considerable thermal distortion. The nature of the distortion is shown in Fig. 32. Two Type C7 wire strain gauges were attached to the weld sample in the position shown in Fig. 32. A similar gauge was attached to a piece of unwelded molybdenum and acted as a temperature compensation leg of the bridge circuit used to measure the strain. Measurements of the resistance of the gauges in the as-welded condition were made and then the sample was sectioned, Fig. 32. Strain gauge resistances were measured after each cut was made. Both of the cuts were made through the line of maximum curvature in the weld specimen. Finally, the strain gauges were cut from the specimen so that only the metal directly under each gauge remained. A reading was taken under these conditions and was used as the condition for minimum stress. The elastic strain was measured and the stresses were calculated. The stresses in the longitudinal and transverse direction were within $\pm 2\%$ of 27,550 psi in absolute value but were opposite in sign. These are the conditions for pure shear. The tensile strength for carbon deoxidized molybdenum at ambient temperature is 55,000 to 60,000 psi and if the shear strength is assumed to be half that value, the stresses in the region of the weld crater approach the strength of the material. Unfortunately, there was not sufficient space on the weld sample tested to place a gauge at 45° so that the direction of the maximum normal stresses could not be calculated. However, the measurements indicate that the stresses in a direction 45° to the direction of the weld could be sufficiently high to cause cracks to develop along this plane. Once a crack has developed at the crater the stress conditions should cause it to continue. Experimental observations showed that the cracks found at the weld crater start at the crater and travel in a direction approximately 45° to the direction of welding. Since the material at the weld crater is usually reduced in section, the stresses at this spot would be higher

than those calculated here because the calculated values were based on the average thickness of the weld test plate. These data indicate that the weld crater cracking encountered in the second lot of carbon deoxidized material was caused by the extremely high values of residual thermal stresses produced in the type specimen used. If, for example, the weld bead had been extended to the edge of the plate, the stresses would probably have been sufficiently reduced so that no cracking would have occurred. If the fracture strength of the material at ambient temperatures had been slightly higher, cracking at the weld crater would not have been observed even when the weld was terminated on the plate. The effect of carbon, discussed earlier, would have given a decrease in ductility for Lot #3 as compared to Lot #1 (Table I) so that more cracking in the 0.04% C, Lot #3, material would be expected as compared to Lot #1, 0.06% carbon.

The residual stress problem in welded joints has always been present. Unfortunately, the problem is often not recognized until cracking occurs. In the case of molybdenum from Lot #1, the stress level in the test pieces was probably the same as was found by measurement on welds from Lot #3. It is probable that the reason cracking was not observed was due to a slightly higher fracture strength at ambient temperature of the material in Lot #1. This difference could be caused by small differences in composition, probably carbon. The difference in strength does not reduce the difficulty; it merely disguises the problem. The need for relieving the stresses in the weld area after welding is apparent from the results obtained with the strain gauge measurements. It is possible that the residual thermal stresses may be relieved by heat treatment at temperatures near 1000°C. This point will require further examination. The heat treatment would have to be done immediately after welding and before cracking could occur. Also, the material welded and the welding conditions should be so adjusted that the stresses do not exceed those required for fracture at the temperatures

encountered after welding. In the particular samples involved in these tests, slight differences in the mechanical properties of the materials appear to have been sufficient to cause one material to be susceptible to cracking to a greater degree than the other. It is probable that additions of alloying elements even in very small amounts could increase the fracture strength of the molybdenum sufficiently to prevent the formation of crater cracks until the material could be stress relieved. It is obvious that any structure fabricated from molybdenum should be so designed that the stresses encountered would be below the level which would cause cracking in the material used, and the welded structure should be stress relieved immediately after welding.

The work on residual welding stresses in the area of the weld crater indicates the need for study of the molybdenum joining problem from the standpoint of the design of the joint and the thermal stresses involved. Improvement of the base material is needed so that the thermal stresses encountered can be tolerated until the weld area may be relieved of the stresses locked in during welding. The best conditions should be determined for relieving the residual welding stresses without involving excessive deformation of the fabricated part. There is also a possibility that residual thermal stresses may be reduced below the level at which cracking will occur by changes in the welding technique such as preheating and changing the welding speed.

C. Diffusion Studies

The possibility of diffusing oxygen and nitrogen from the weld zone into the parent plate was first examined from the viewpoint of the data available in the literature. If sufficient diffusion occurred, it could be possible to weld in atmospheres of commercial argon and reduce the nitrogen and oxygen by post weld diffusion treatment.

Unfortunately, the diffusion data for oxygen and nitrogen are not plentiful in the literature and the agreement between independently reported results is not good. However, such data as were available were used to determine the advisability of diffusion treatment as a possible method of improving the ductility of the molybdenum weld metal.

Nitrogen diffusion calculations were made using the data found in the literature for diffusion coefficients to determine the temperature and diffusion time which would give the best results with respect to removal of nitrogen from the weld.^{6,7,8} Unfortunately, there is wide variation in the values available. Data from the Battelle Memorial Institute⁸ gave $Q = 76000$ cal/mole for diffusion of nitrogen in molybdenum. No value for D_0 is given. Norton and Marshall⁹ gave $Q = 26600$ cal/mole. There was some doubt about the Battelle data since this work was done by internal friction and the nitrogen in the molybdenum was largely located in a case on the surface. For this reason, it was decided to use the data of Norton and Marshall.⁹ Since no value for D_0 was available in either set of data, a value of 0.1 was assumed. Using the conventional diffusion rate equation, $D = D_0 e^{-Q/RT}$, values of D were found for several temperatures, Table XIII.

TABLE XIII
VALUES OF D AT SEVERAL TEMPERATURES FOR
DIFFUSION OF NITROGEN IN MOLYBDENUM

<u>Temperature °C</u>	<u>D*</u>
1000	7.587×10^{-5}
1200	3.126×10^{-4}
1500	1.906×10^{-4}
2000	3.631×10^{-3}

*Based upon assumed values of D_0 .

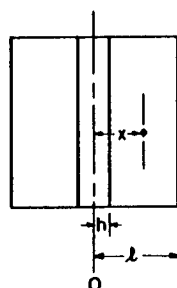
The boundary conditions for the weld test plate are shown in Fig. 33. The equation for diffusion of gases through metals under these conditions is given by Barrer:¹⁰

$$C = C_0 \left(\frac{h}{l} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} e^{-(n\pi/l)^2 Dt} \cos \frac{n\pi x}{l} \sin \frac{n\pi h}{l} \right) \quad (1)$$

t = time in seconds

C = final concentration

For values of h, l, λ, and C₀, see Fig. 33.



DWG. 57-D-6773

When:

x = 0 to h C = 0.05 % N

h < x < l C = 0.003 % N

Weld Dimensions:

h = .254 Cm.

l = 2.54 Cm.

Using the boundary conditions shown above and in Fig. 33 and assuming a temperature for diffusion of 1000°C and two different values of t, the results in Table XIV were calculated.

Fig. 33 - Diffusion Boundary Conditions for Nitrogen in Molybdenum Welds

TABLE XIV
CALCULATED DIFFUSION CONCENTRATIONS IN WELDS
AFTER HEAT TREATMENT AT 1000°C

<u>Time-Sec.</u>	<u>For Original Nitrogen Concentration</u>	<u>Final Nitrogen Concentration</u>
1000	0.050%	0.020%
10000	0.050%	0.007%

These calculations indicate that it may be possible to diffuse nitrogen from the weld into the parent metal at 1000°C in about 2.77 hrs. Both the time and temperature are within reasonable limits. The temperature is below the recrystallization temperature for molybdenum. These data are at best a rough estimate of the nitrogen concentrations when firm values of Q and D₀ are lacking.

Oxygen diffusion is desirable so that the oxygen concentration in the weld will be reduced at the expense of the plate. Values of Q and D_0 for the diffusion of oxygen in molybdenum were not readily located in the literature so that these values were calculated from data published by Battelle.¹¹ Their data showed that at 3500°F (1928°C) the oxygen concentration in a 1/4" diameter bar was reduced from 0.0011 to 0.0002% in three hours. Barrer gives equation (2) for diffusion under these conditions.¹⁰

$$\bar{C} = \frac{4 C_0}{a^2} \sum \frac{1}{2n} e^{-Dt\alpha_n^2} \quad (2)$$

$$\alpha_1 = \frac{2.405}{a}, \alpha_2 = \frac{5.520}{a}, \alpha_3 = \frac{8.654}{a}, \alpha_4 = \frac{11.791}{a}$$

\bar{C} = final concentration

C_0 = initial concentration

t = time, sec.

a = radius in cm.

Using this equation and a method of approximation, the value of D at 1928°C was found to be 1.635×10^{-5} . From the rate equation $D = D_0 e^{-Q/RT}$ and assuming $D_0 = 1$, the value of Q was found to be 48300 cal/mole. Using these values for Q and D_0 , the values of D were calculated for several different temperatures, Table XV.

TABLE XV
VALUES OF D AND TEMPERATURE FOR
OXYGEN DIFFUSION IN MOLYBDENUM

<u>Temp. °C</u>	<u>D</u>
1000	5.43×10^{-10}
1200	7.5×10^{-8}
1500	1.2×10^{-6}
2000	2.48×10^{-5}

Using the same general diffusion arrangement shown in Fig. 33, and starting with an oxygen concentration in the plate of 0.0018% and an oxygen concentration in the weld of 0.004%, the times and temperatures required to obtain oxygen concentrations in the weld zone approaching that of the plate were calculated. In this calculation a value of C_0 equal to 0.004 - 0.0018 or 0.0022 was used in order to use equation (1) in the diffusion calculations. The results of these calculations are given in Table XVI.

TABLE XVI
CALCULATED OXYGEN CONCENTRATIONS IN THE WELD AFTER DIFFUSION

<u>Temp. °C</u>	<u>Time - Seconds</u>	<u>Oxygen Concentration in the Weld</u>	
		<u>Before Diffusion:</u>	<u>After Diffusion</u>
2000	10^3	0.004	0.00288%
2000	10^4	0.004	0.0024%

Calculations at 1000°C indicated that the diffusion equations were not applicable at this low temperature and that no diffusion could be expected. However, the data indicate that reasonable success in diffusing oxygen from the weld zone will be achieved at temperatures of 2000°C. Diffusion treatment at this temperature for the time required (2.77 hrs.) would cause sufficient grain growth in the molybdenum parent metal to cause a loss in ductility due to the grain size effect. This loss in ductility might well outweigh the improvements obtained in the weld by reduced oxygen concentrations.

The diffusion calculations made and reported here indicate that some improvement of the weld ductility may be obtained by heat treating welds at 1000°C in a vacuum or completely inert atmosphere. However, the improvement would be due only to the reduction in the nitrogen concentration in the weld since the amount of oxygen diffusing at this



Fig. 34 - Sections for Diffusion Tests, Weld Made Under Welding Grade Argon in Aluminum Deoxidized Material, Sample Al-5

temperature is insufficient to show much improvement. If temperatures sufficiently high to reduce the oxygen concentration are used, excessive grain growth of the weld and unfused plate will result and may tend to obliterate

the improvement gained through changes of chemical composition.

Nitrogen diffusion tests were conducted to determine the validity of the calculations. Test welds were made using welding grade argon since previous studies² had indicated that the expected nitrogen content of welds made under welding grade argon would contain nitrogen in the range 0.020 to 0.050%. The test welds were made in molybdenum from Lots #2 and #3 deoxidized with 0.16% Al and 0.04% C. A number of welds were made in each material so that the diffusion rates could be examined at different temperatures. A typical weld is shown in Fig. 34. The method of sectioning these welds for the diffusion tests is shown in that figure. Only the three center sections were used. Sections 2 and 4 were used as the diffusion samples at a given temperature and two different lengths of time. Section 3 was used as a control.

The first exploratory heat treatment for diffusion was done at 1000°C for 0.277 and 2.77 hrs (1000 and 10000 seconds). The width of the weld area and the distance to the edge of the plate were measured prior to treatment. After the diffusion heat treatment in vacuum the weld area was milled out for chemical analysis. The chips were taken from the center of the weld and the cut width was 1.9 mm. Chips were milled from the edge of the test plate in a cut 6 to 7 mm deep. The chips were analyzed for nitrogen content and the results are given in Table XVII. Some diffusion may have taken place. However, the amount of diffusion seems to be less than the calculated values indicated. There is also scatter in the nitrogen data. Sample G-48 showed a greater nitrogen

TABLE XVII
NITROGEN DIFFUSION DATA

Sample	Section	Diffusion Treatment		Diffusion Distance cm	Nitrogen Analyses	
		Temp. °C	Time Hrs		Weld %	Sample Edge %
G-48	3	None	-	-	0.008	0.001
G-48	4	1000	2.77	2.02	0.011	0.003
G-48	2	1000	0.277	2.06	0.013	0.006
Al-5	3	None	-	-	0.016	0.003
Al-5	4	1000	2.77	2.07	0.013	0.007
Al-5	2	1000	0.277	2.01	0.003	-
G-48	3	-	-	-	0.008	0.001
G-48	2	1000	0.277	-	0.013	0.006
G-48	4	1000	2.77	-	0.011	0.003
G-51	4	-	-	-	0.0068	0.003
G-51	5	1200	0.277	-	0.0025	0.0038
G-51	3	1200	2.77	-	0.0046	0.0054
G-52	3	-	-	-	0.006	0.003
G-52	2	1400	0.277	-	0.008	0.009
G-52	4	1400	2.77	-	0.0071	0.0059
Al-5	3	-	-	-	0.016	0.003
Al-5	2	1000	0.277	-	0.008	-
Al-5	4	1000	2.77	-	0.013	0.007
Al-8	4	-	-	-	0.0098	0.0084
Al-8	3	1400	0.277	-	0.0104	0.046
Al-8	2	1400	2.77	-	0.0109	0.0047

concentration in the weld in the diffusion treated state than in the control sample. The nitrogen concentration in the weld metal prior to heat treatment was not as high as was expected from some of the data collected in previous investigations.² However, the increase in the nitrogen concentration at the edge of the sample in each case indicates that some diffusion had occurred during heat treatment at 1000°C. It appeared that if calculations for the diffusion of nitrogen from the weld zone were to be made that these results would have to be rechecked. A calculation of the values for D_0 based on the value of Q at 26600 cal/mole indicates that for the aluminum deoxidized sample treated for 2.77 hrs at 1000°C, the value of D_0 was 0.1075. However, the results for the sample treated for 0.277 hrs show

the D_0 value to be 3.5, a difference of more than an order of magnitude.

Several more samples were prepared and heated in vacuum at 1200 and 1400°C. The data are given in Table XVII. These results showed the same degree of scatter encountered in the earlier tests. During the search for an explanation of the difficulties encountered in the nitrogen diffusion tests, a series of analyses were made from samples taken at different locations across the original unwelded strip. These analyses showed a nitrogen gradient which varied from 0.0017 to 0.0047, Fig. 35. It seems probable that this difference in nitrogen concentration in the original material could have caused at least some of the

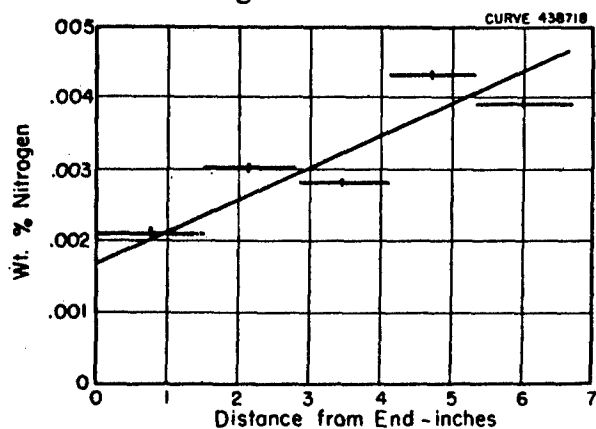


Fig. 35 - Sheet 0.04% C Deoxidized Molybdenum, Lot #3.

scatter encountered in the diffusion data. It was not possible to apply a correction factor to the diffusion data because the direction of the nitrogen gradient in the sample before welding could not be determined. The diffusion data may be further confused by a tendency for a zone refining action due to the

passage of the fusion zone along the test plate. The data obtained from the diffusion tests show some qualitative indication of reduction of nitrogen in the weld zone but quantitative data on the diffusion constants cannot be computed from these data. In general, the nitrogen diffusion data obtained in these particular tests were inconclusive.

D. Heat Treatment

Studies of the effects of heat treatment on molybdenum welds have been divided into two phases. The effects of aging treatments on precipitated particles were explored and the possibility of straining at

elevated temperatures and using heat treatment to produce a fine grain effect by polygonization is being investigated. An attempt was made to deliberately overage precipitated particles so that they will be in a form which can cause the least damage to the ductility of the material.

Overaging studies were begun by using a 0.04% carbon deoxidized sample welded under purified argon. This weld was sectioned as indicated in Fig. 36. Sample strips from the weld were heat treated in vacuum at 400, 800, 1000, 1200, 1600 and 2000°C. The first exploratory tests were made for 1 hr periods and the samples were examined metallographically for precipitate formation. Photomicrographs of these samples are shown in Fig. 37. Metallographic examina-

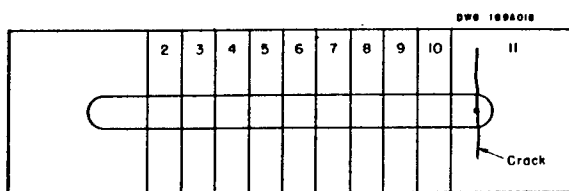
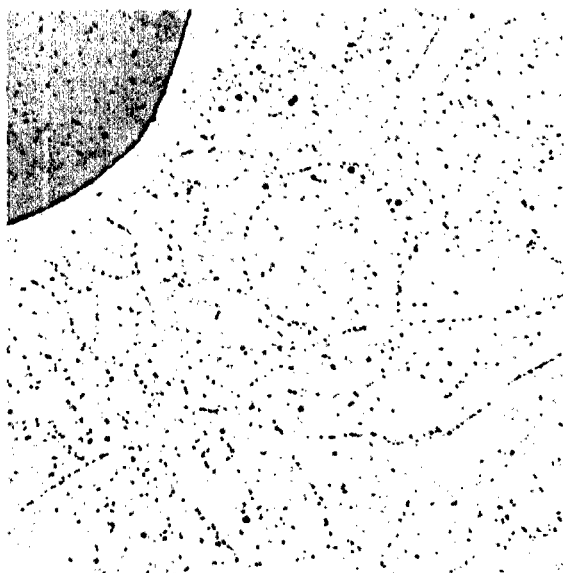


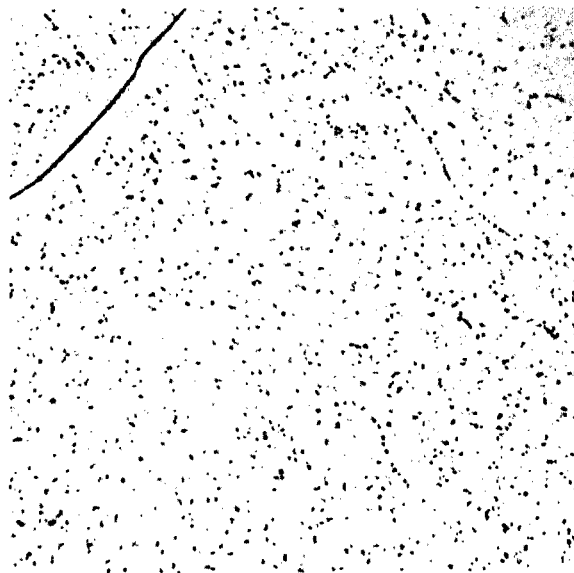
Fig. 36 - Sections for Heat Treatment, Weld PAC10 Made Under Purified Argon

tion of the weld areas shown in this figure indicated that the as-welded samples showed a precipitate in the grain matrix and in the grain boundaries. A very fine precipitate was also observed

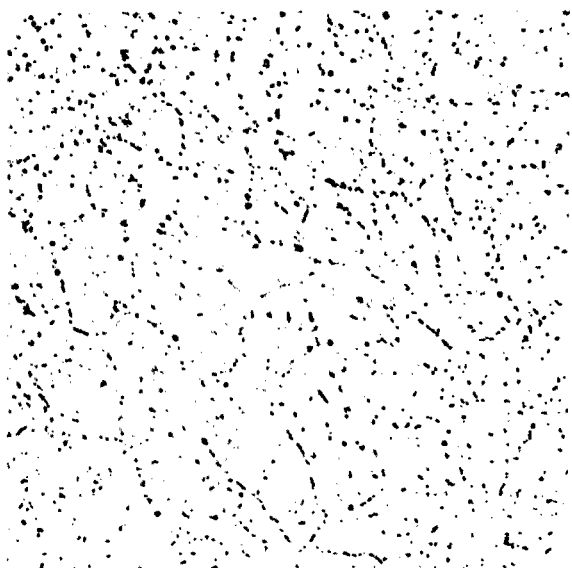
in the background in the grain matrix. This background precipitate could not be resolved at 300X. As the heat treating temperature increases from 400°C to 1000°C, the precipitate in the grain matrix becomes heavier with a more general dispersion apparently at the expense of the fine background of unresolvable precipitate. The beadlike network of precipitates in the grain boundaries becomes more nearly complete with increasing temperatures up to 1200°C. At 1200°C, the density of the matrix precipitates decreases with most of the remaining precipitate being located in subgrain boundaries. Apparently some of the precipitate has returned to solution. At 1600° to 2000°C the precipitate shows a marked decrease and the boundary films have almost disappeared. The wide grain boundaries shown in Figs. 37(f) and 37(g) are caused by a difference in the height of



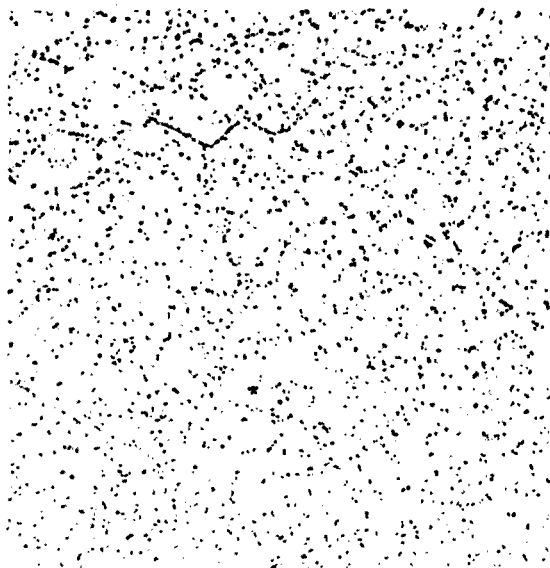
(a) As Welded - 300X P56-23-1



(b) 400°C - 300X P56-23-3

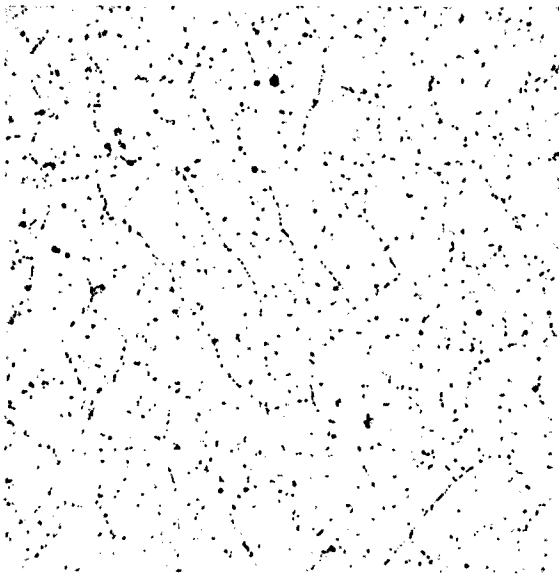


(c) 800°C - 300X P56-23-4

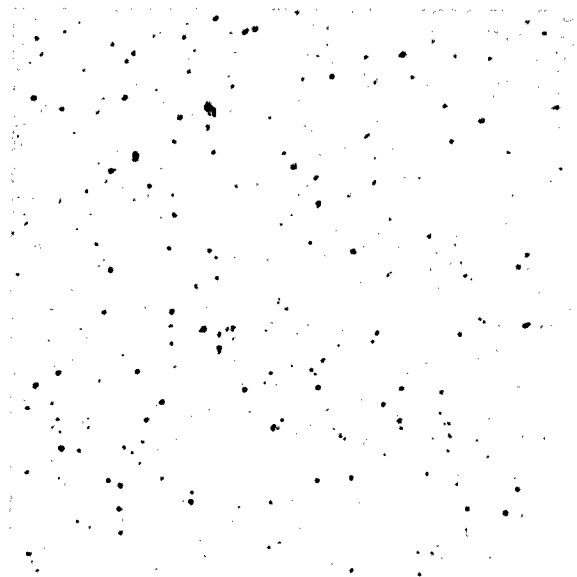


(d) 1000°C - 300X P56-23-5

Fig. 37 - Welds in Arc-Cast 0.04% C Deoxidized Molybdenum Made Under Purified Argon Heated One Hour at Various Temperatures.



(e) 1200°C - 300X P56-23-2



(f) 1600°C - 300X P56-23-6

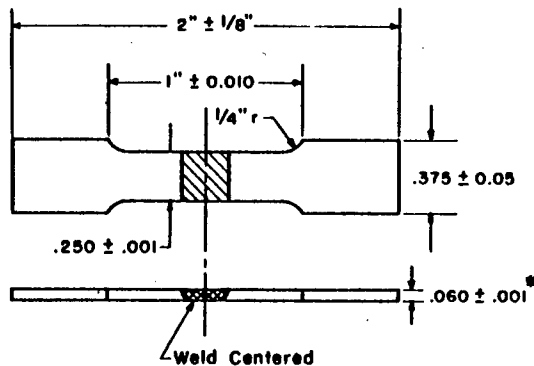


(g) 2000°C - 300X P56-23-7

Fig. 37 - Welds in Arc-Cast 0.04% C Deoxidized Molybdenum Made Under Purified Argon Heated One Hour at Various Temperatures.

the grains due to the electropolishing technique used. From the metallographic examination, it appears that the precipitate formed during welding will start to go back into solution at 1200°C and was almost completely in solution at 2000°C. The grains in the unfused parent metal show evidence of secondary grain growth starting at 1200°C. It is also interesting to note that the grain size of the weld metal did not increase with increasing heat treating temperature as did the unfused material. In many cases the grains in the fused material were smaller than those found in the parent plate after heat treatment. The metallographic observations indicate that the material should show some overaging effects in the grain matrix at treating temperatures of 1200°C. However, improving the ductility by this technique seems doubtful since the boundary precipitate is near its maximum at 1200°C, but in the absence of any mechanical test data, it seems advisable to make exploratory mechanical tests of heat treated welds.

The nature of the precipitate observed in Fig. 37 is not known; however, it is possible that both carbides and nitrides are present. Data from Frew and Manning¹⁰ show that at 2000°C the solubility of carbon in molybdenum is approximately 0.015%. These data do not indicate the possibility of putting the carbides into solution as shown in Fig. 37(g) since the base material contained 0.04% carbon. Previous analyses of weld metal indicate that the carbon content in the weld metal is not changed from that of the original unfused material. These facts suggest that carbides should be present and that they should not go into solution at the temperatures used in these experiments. However, the data shown in Fig. 37 are not in agreement with these deductions and some other explanation must be sought. Examination of the molybdenum-nitrogen system added little to the information since nitrides should be present at temperatures below 1000°C but data on this system were not found above 1000°C.¹¹



*Note: Grind to clean up welds. Hold samples in any group of specimens to ± 0.001 "

Fig. 38 - Polygonization Specimen

zation in the weld metal. It is hoped that a fine grain effect will be produced by this process.

A weld specimen was made in arc-cast 0.04% carbon deoxidized molybdenum and machined into tensile specimens. The specimens were made with the weld perpendicular to the direction of loading, Fig. 38. It was proposed that the specimens be prestrained at 650, 870 and 1100°C. Unfortunately, it was found that existing fixtures for the tensile equipment were inadequate at the temperatures required for prestraining the welds prior to polygonization. Failure of the tensile test grips made it necessary to redesign fixtures so that the specimens could be strained. The changes required in the tensile fixtures also required a change in the specimens such that a new set of test specimens were required for polygonization tests. The new test fixture is shown in Fig. 39. This fixture has been partly completed and will be used in future test work. The specimens were modified so that the new holders could be used, Fig. 40. The specimens are designed so that they will be loaded along the radius in a manner similar to a conventional button head round tensile specimen. The grips, Fig. 39, were designed to prevent buckling when tensile loads are applied.

Several welds were made using purified argon. These welds were also machined into tensile specimens as shown in Fig. 40. These

Polygonization studies

have been started. It is believed that the grain orientation in the weld is such that the application of tensile stresses normal to the direction of welding will produce some bending in the grains. If this is the case, subsequent heat treatment at 1500 to 1600°C should produce some polygani-

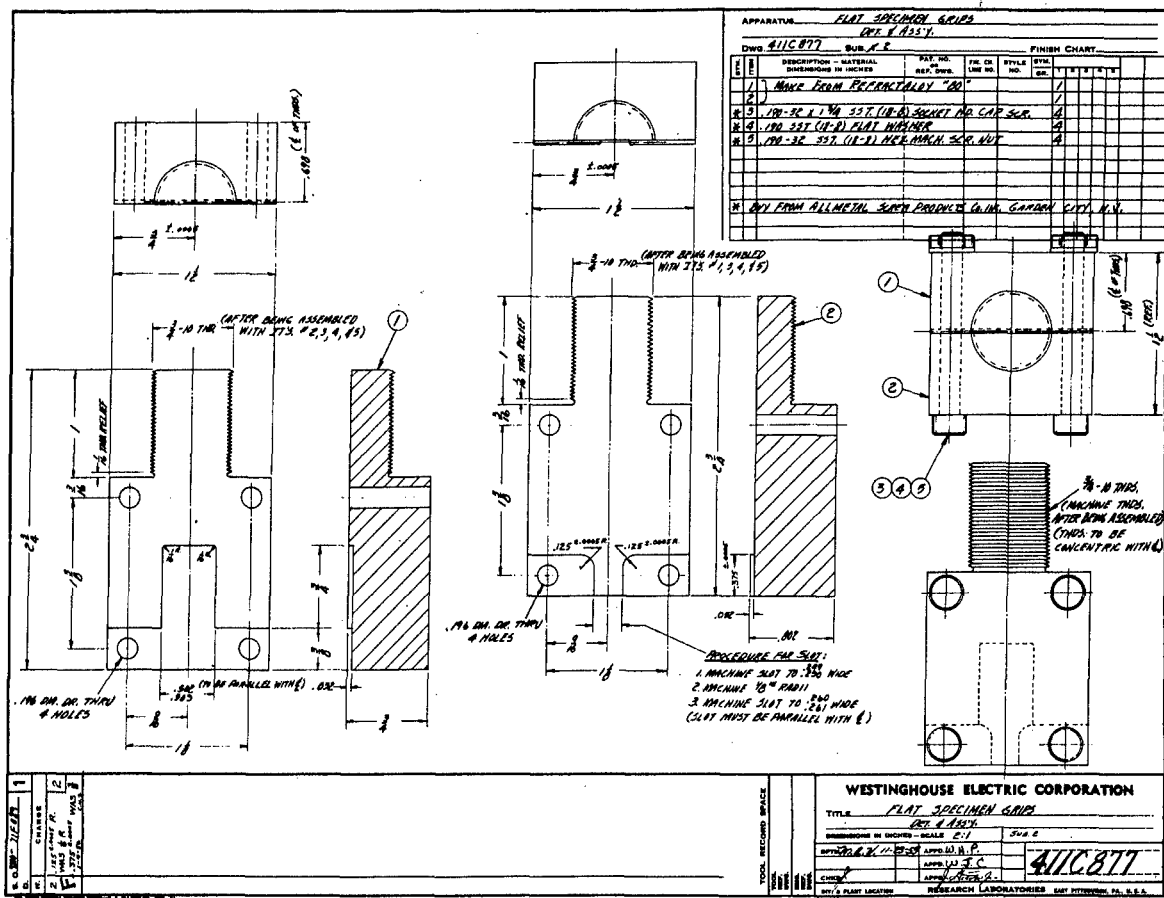
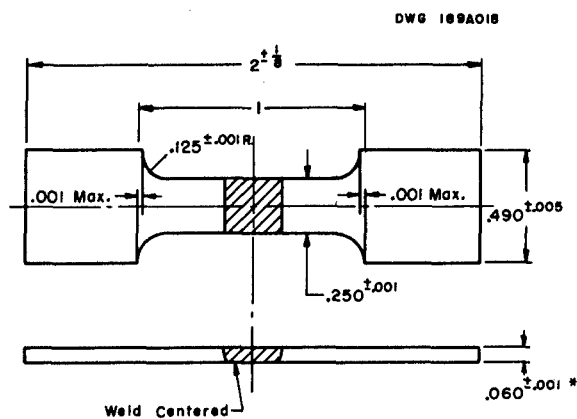


Fig. 39 - Flat Specimen Grips



Note: *Grind to Clean Up Weld. Hold Samples
In Any Group of Specimens to $\pm .001$
Clean Off Burrs. Dimensions in Inches.

Fig. 40 - Tensile Specimen

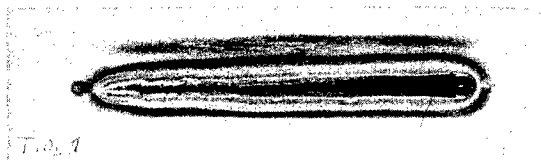


Fig. 41 - Weld Made Under Welding Grade Argon With TiO_2 on Surface

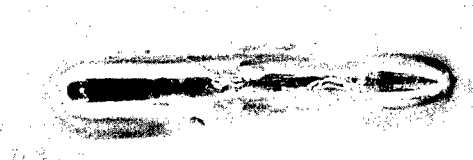


Fig. 42 - Weld Made Under Welding Grade Argon With Titanium Powder on Surface

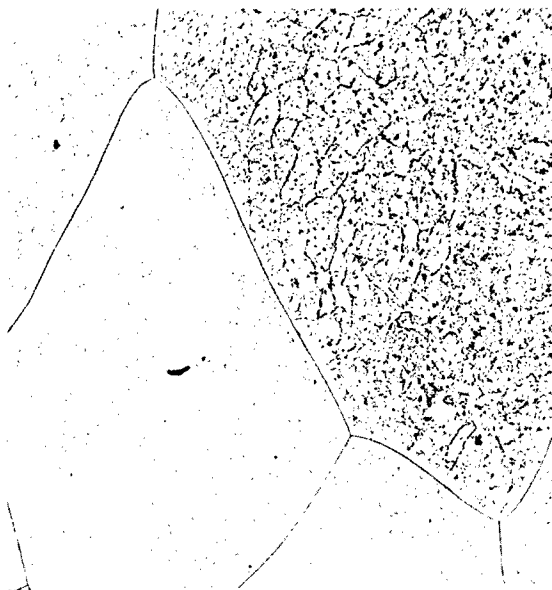


Fig. 43 - Weld Zone in 0.04% C Deoxidized Molybdenum. Made Under Welding Grade Argon. TiO_2 Powder on Surface of Weld Plate. 100X P-56-22-1

samples will be strained over a range of temperatures and then heated to $1500^{\circ}C$ for a short period of time to polygonize the material. The test fixtures and specimens are completed but actual testing has not yet begun.

E. Weld Metal Additions

The possibility of reducing the grain size in the weld metal and improving ductility by additions of metallic and non-metallic particles is being considered.

Two exploratory tests were made in which powdered material was added to the welds by placing it on the surface of the test plates before the welds were made. TiO_2 was added in one case and titanium powder in the other. Past experience had shown that titanium additions had reduced the weld grain size, and it was thought that the grain size was restricted by the titanium oxide particles formed during the deoxidization process. It was also thought that additions of foreign materials could act as

nucleation centers during solidification and further reduce the grain size in the weld metal.

Photographs of welds made using titanium dioxide and titanium powder on the surface of the plate are shown in Figs. 41 and 42. The external appearance of these samples is very poor. However, since these tests were only exploratory in nature, the appearance will be neglected and the effect on the microstructure will be considered. These welds were given metallographic examination and Fig. 43 shows the grain size at the center of the weld area. The grain size does not appear to be reduced by the addition of TiO_2 to the weld metal by the method of coating the surface prior to welding. The weld made using Ti powder additions showed results similar to those obtained using TiO_2 . The exploratory study indicates that reduction of weld grain size by additions to the fused metal during welding will not be successful.

IV WORK WITH SINTERED MOLYBDENUM

Two welds were made in 0.2% zirconium deoxidized vacuum sintered molybdenum which had been made under a separate project at the Westinghouse Research Laboratories. Welding grade argon was used as the welding atmosphere for these welds. The welding data are given in Table XVIII.

TABLE XVIII
WELDING DATA VACUUM SINTERED MOLYBDENUM

<u>Sample</u>	<u>Atmosphere</u>	<u>Welding Current</u>	<u>Welding Voltage</u>	<u>Arc Travel Speed</u>	<u>Comments</u>
WS248A	Welding Grade Argon	180	13	6"/Min	Clean, bright weld, no cracks.
WS248B	Welding Grade Argon	182	14	6"/Min	Clean, bright, cracked before removed from chamber. Thermal distortion.

Photographs and X-ray pictures of the welds are shown in Fig. 44. One weld was cracked before it could be removed from the welding chamber. The other sample was free of cracks and porosity. Typical photomicrographs of the as-rolled and the fused metal in the weld are shown in Fig. 45. The inclusions in the material are probably zirconium oxides. These oxides seem

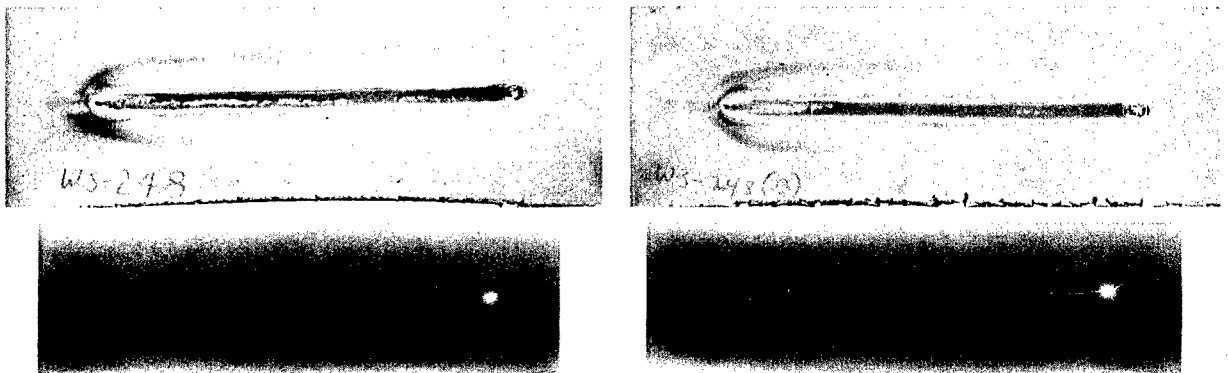
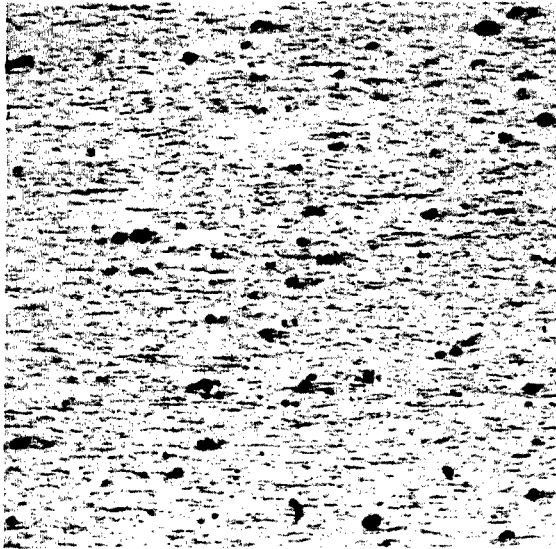
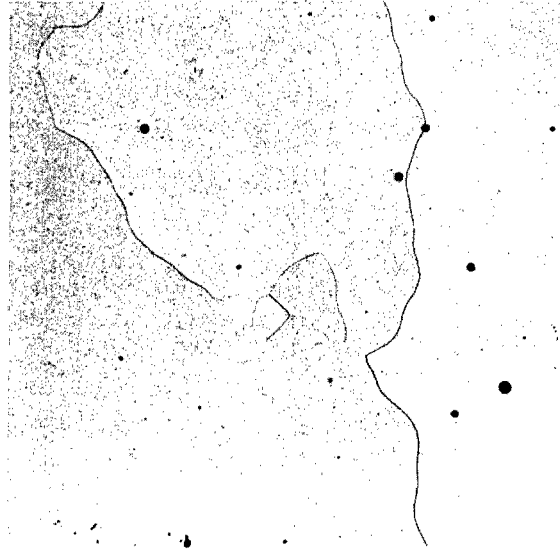


Fig. 44 - Radiographs and Photographs of Weld in 0.2% Zr Deoxidized Vacuum Sintered Molybdenum. Argon Atmosphere.
WS248A,B - R-13289, R-13291

to be unaffected by the fusion of the molybdenum. This condition was expected since the melting points of the oxides of zirconium are both above the melting point of molybdenum. However, the melting point of zirconium is only 1900°C and any zirconium remaining in the material could, by a coring action, be concentrated in the grain boundaries. This could



P55-107-1
(a) As Rolled



P55-107-2
(b) Weld Zone

Fig. 45 - 0.2% Zr Deoxidized Vacuum Sintered Molybdenum, Welded in Argon. WS248

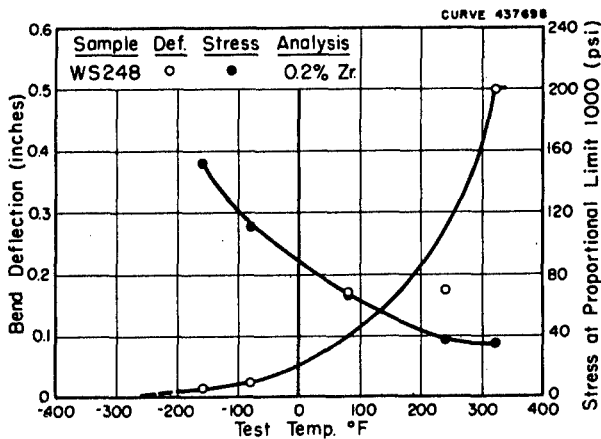


Fig. 46 - Weld in Vacuum Sintered Zr Deoxidized Molybdenum. Made Under Argon Atmosphere

cause low intergranular cohesion which may result in the hot cracking found in this material.

One of the welds in zirconium deoxidized molybdenum was tested in bending and the data are shown in Table XIX and Fig. 46. The weld in this material was ductile at 320°F and completely brittle at -250°F. The ductility is roughly the same as found for welds in carbon deoxidized arc-cast molyb-

denum. This material is subject to bead and crater cracking since one of the two original samples showed a crack which originated at the crater and

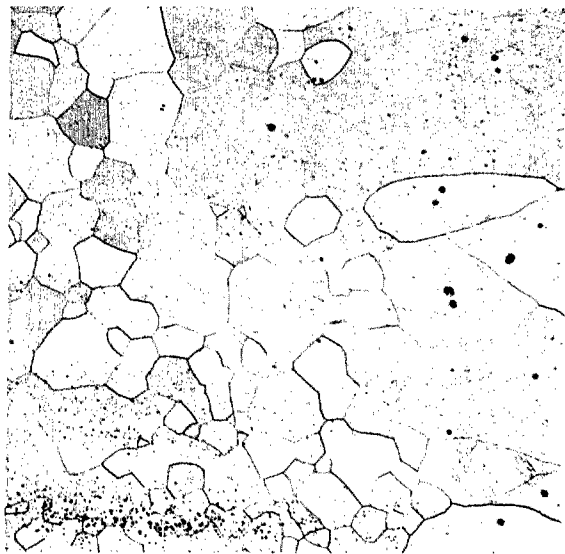
TABLE XIX
BEND TEST DATA
WELD MADE UNDER ARGON ATMOSPHERE IN ZIRCONIUM
DEOXIDIZED ARC-CAST MOLYBDENUM

<u>Sample</u>	<u>Test Temp.</u> <u>°F</u>	<u>Deflection Rate</u> <u>In/Hr</u>	<u>Stress at Propor-</u> <u>tional Limit, PSI</u>	<u>Bend Deflection</u> <u>Inches</u>
WS248	320	6	34,800	0.500*
	240	6	37,000	0.171
	80	6	66,600	0.169
	- 80	6	111,000	0.020
	-160	6	152,000	0.014

*Maximum deflection - no fracture.

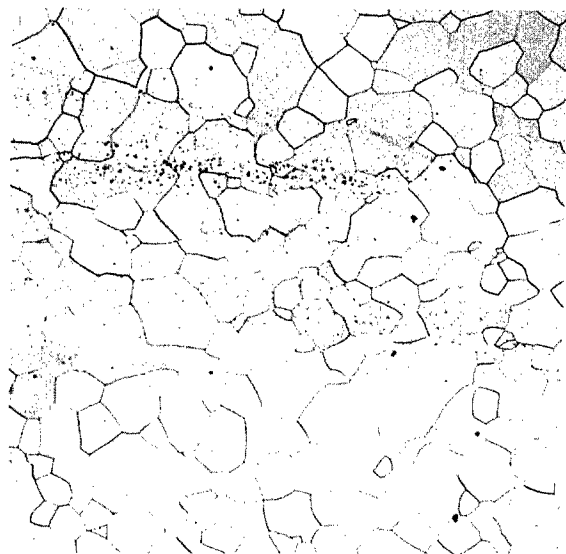
extended approximately one-third the length of the weld bead.

Investigations reported earlier on the use of titanium as a deoxidizer for molybdenum² have shown that titanium powder must be protected when it is added to molybdenum before sintering. At that time, it was reported that additions of titanium powder were most effective when the powder was added wet. The water content, while it protected the powder, prevented uniform mixing of the titanium with the molybdenum. Attempts to improve the mixing by drying the powder were found to be unsuccessful in proportion to the degree of drying attained. Attempts were made to improve the uniformity of titanium deoxidized vacuum sintered molybdenum by mixing in a slurry of volatile solvents. Three samples were mixed in a slurry of acetone for 30 to 120 seconds and then the acetone was evaporated and the sample was pressed and sintered. A control sample was made using wet titanium powder and welded under the same condition as the acetone mixed material. It was apparent from the appearance of these samples after welding that mixing in acetone is not successful with respect to preventing porosity. Metallographic samples were made to determine if any improvement in the mixing was obtained. Photomicrographs



P-56-22-3

(a) Edge of Weld - 100X



P-56-22-2

(b) Unfused Metal - 100X

Fig. 47 - Weld in Vacuum Sintered Molybdenum Deoxidized With 0.2% Ti
Added Wet - WS165

of the edge of the weld zone and a portion of the unfused parent metal are shown in Figs. 47-50. Areas were chosen which showed the poorest mixing in the sample so that the extent of mixing must be considered on this basis when examining the photomicrographs. It is apparent from the photomicrographs that mixing in the acetone slurry did not improve the homogeneity of the material. The weld porosity found in the samples mixed in the acetone slurry indicates that the titanium powder was not sufficiently protected during the mixing operation to permit it to be successful as a deoxidizer. Mixing in an acetone slurry seems to be impractical at present but past experience with deoxidization of sintered molybdenum suggests that such mixing may be possible with slight changes in the mixing technique.

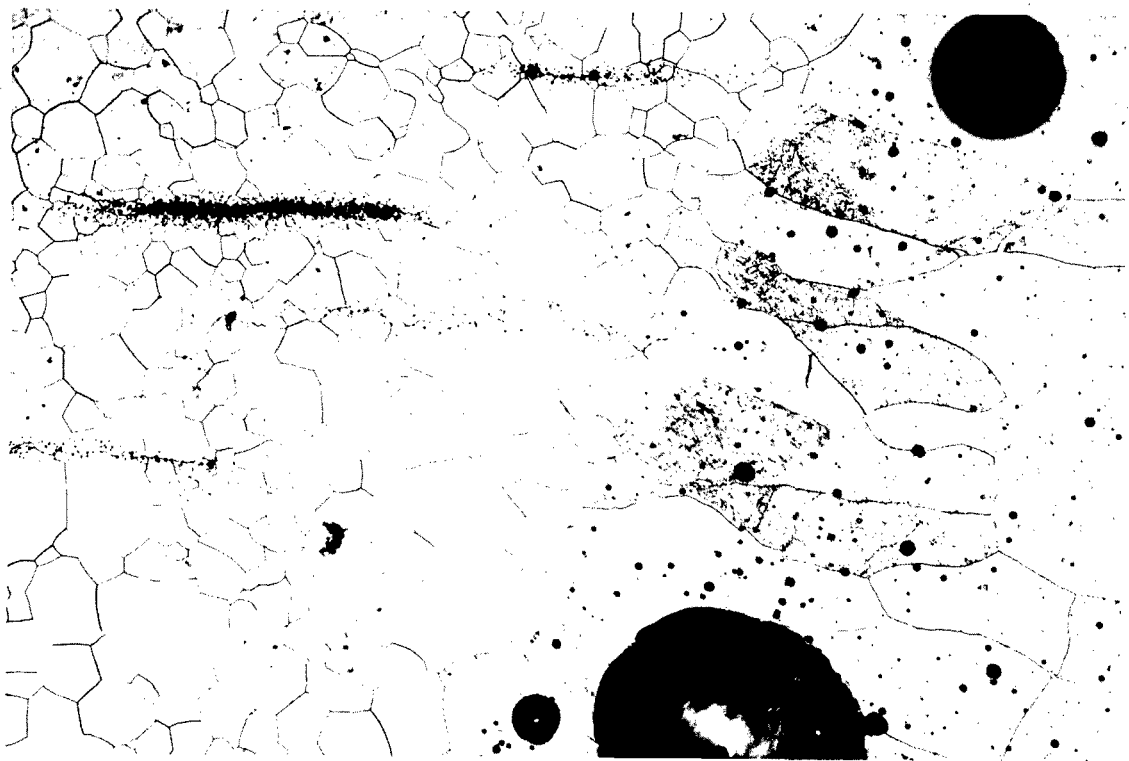


Fig. 48 - P-56-22-6 - 100X - Weld in Vacuum Sintered Molybdenum
Deoxidized With 0.2% Ti Mixed in Acetone Slurry 30 Seconds - WS269

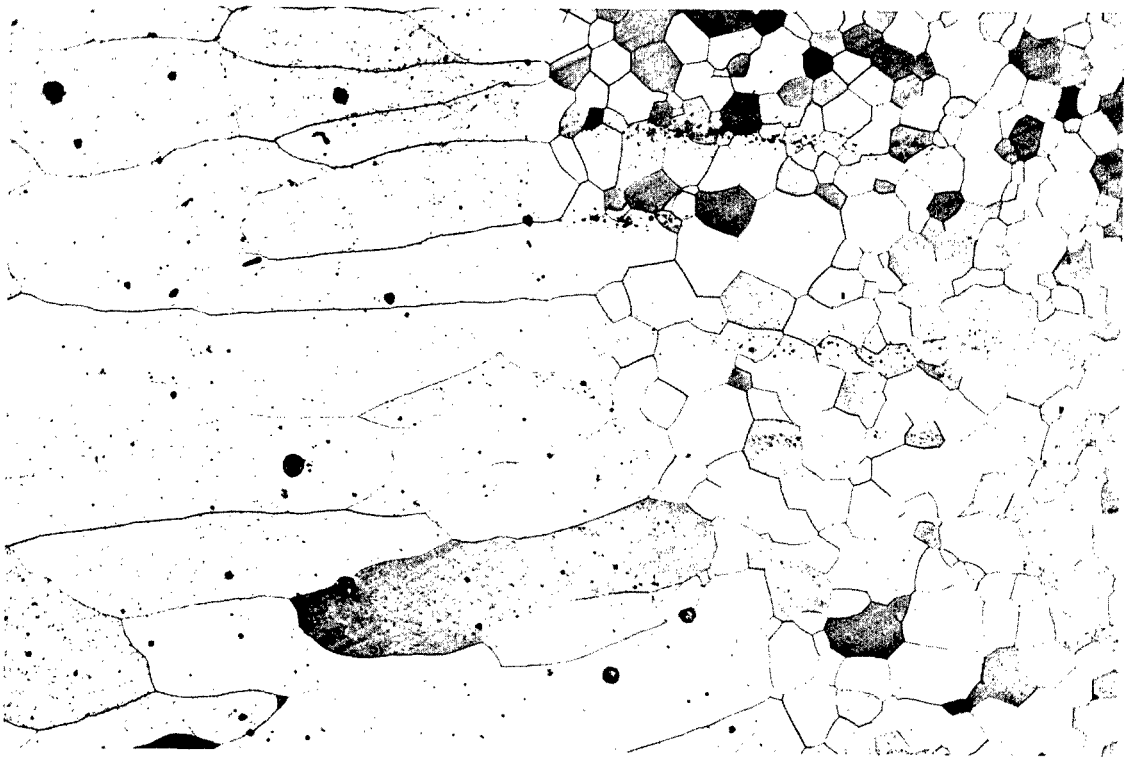
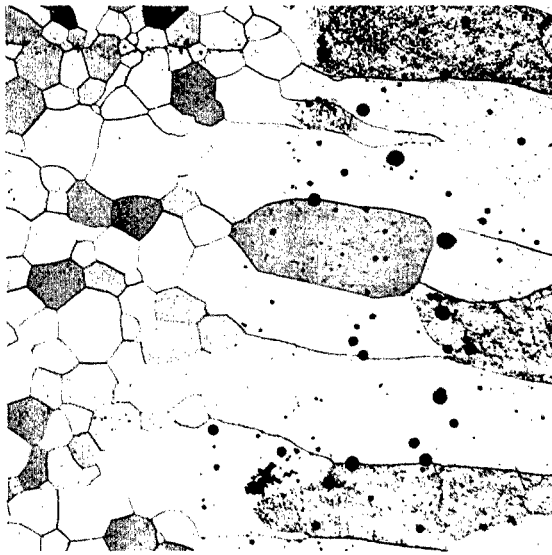
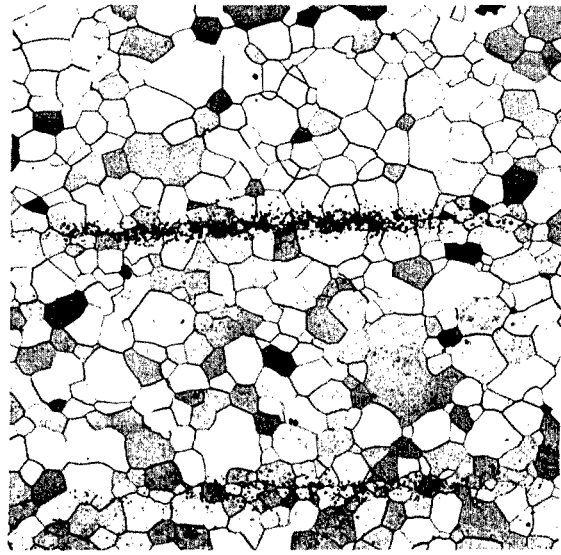


Fig. 49 - P-56-22-7 - 100X - Weld in Vacuum Sintered Molybdenum
Deoxidized With 0.2% Ti Mixed in Acetone Slurry 60 Seconds - WS271



P-56-22-4 - 100X
(a) Edge of Weld



P-56-22-5 - 100X
(b) Unfused Plate

Fig. 50 - Weld in Vacuum Sintered Molybdenum Deoxidized With 0.2% Ti Mixed in Acetone Slurry 120 Seconds - WS272.

V SUMMARY

The work on welding atmospheres shows that the amount of oxygen and nitrogen acquired by the molybdenum weld metal can be reduced to a minimum by using purified argon or helium. The welds made under these purified atmospheres show no increase in oxygen or nitrogen content over the unfused base plate. However, the improvement in ductility due to the use of purified atmospheres is relatively small. The greatest improvement was observed in the case of 0.46% Ti deoxidized molybdenum where the temperature for ductile behavior (120° bend) was decreased 40°F. The improvement in the other materials was not great enough to be detected by the bend test method used. However, it would seem wise to purify or maintain a close quality control

check on the welding atmospheres used with molybdenum so that variation in the quality of commercial inert gases will not cause oxygen or nitrogen contamination beyond the concentration in the parent metal.

The ductility data from the five different lots of arc-cast molybdenum indicated that the effect of deoxidizing or minor alloy additions is larger than the effects of atmosphere purification. The data indicate improvement in the ductility under a given set of welding conditions with increased carbon content. However, these data are not sufficiently complete to justify firm conclusions since only two carbon contents are represented. It would be advisable to examine the welding properties of molybdenum in the range between 0.06% to 0.1% carbon. Deoxidizers examined other than carbon improve the ductility. For example, Ti and Al decreased the temperature for ductile behavior by at least 100°F over material with similar carbon content. The best properties obtained thus far in these investigations were found for 0.46% Ti, 0.05% C deoxidized material. This material was ductile at 80°F. Aluminum deoxidized material was ductile at 120°F as compared to 0.06% carbon deoxidized molybdenum which was ductile at 200 to 300°F. Two lots of 0.5% titanium deoxidized molybdenum were examined and the difference in carbon content of 0.015 to 0.05% indicated that with titanium deoxidization an increase in the carbon content improved the ductility of the weld metal. These data indicate that the effect of alloy additions should be investigated so that an alloy of molybdenum which is suitable for welding may be selected while the other properties required for use in structures are not neglected.

In the course of the investigations on molybdenum joining, metallographic examinations have indicated that the materials which have low oxygen and nitrogen contamination combined with an alloying element such as titanium or aluminum show the best ductility and also show the least amount of grain growth in the unfused material adjacent to the weld metal. The combination of these conditions tends to reduce the grain size of the

weld metal. If the contaminating materials are in the grain boundaries, then for a given contamination concentration as the grain size decreases the boundary film will be less likely to be continuous. It was shown previously² that the failure in weld metal originated in almost all cases at the grain boundaries. Hence, any improvement in the ductility of the weld metal should stem from a decrease in the continuity of the boundary contamination causing failure. One means of breaking up the boundary films is to reduce the grain size which increases the boundary area available per unit volume. Hence, the boundary films may become discontinuous and the ductility will be improved. Any means which leads to a decrease in the grain size of the weld metal should tend to improve the ductility. Metallographic observation has shown that in general when the grain size of the unfused material adjacent to the weld metal is small, the grain size of the weld metal will be reduced accordingly. This condition suggests that any addition to the molybdenum which will restrict the grain growth in the unfused material will decrease the weld metal grain size. It is strongly suggested that the program of alloy development be directed first toward alloying elements which restrain the grain growth and increase the recrystallization temperature.

The large values obtained for the residual welding stresses in the molybdenum test plates indicate the need for some means of post-weld stress relief of the weld metal. It was obvious that the residual stresses reached the fracture stress of the material in the area of the weld crater and produced cracking. The actual measurements of a sample which did not crack confirmed the existence of residual welding stresses. The observed difference between the extent of crater cracking in molybdenum Lots #1 and #3, 0.06 and 0.04% C, indicated that a material which has a better degree of ductility at room temperature is less likely to crack after welding. It is believed that the development of new alloys which have better ductility at room temperature will reduce the tendency toward crater cracking. However, it is obvious that some means of removing or

preventing residual welding stresses is needed. Thermal treatment should be investigated as a means of relieving welding stresses. Design of welded joints so that welding stresses are held at a minimum should also be investigated. A study of welding heat distribution and dissipation should also prove helpful.

The diffusion of nitrogen from the weld metal into the parent plate by post-weld thermal treatment has not been firmly established by the experimental work described. Although the calculations based on data obtained from the literature indicated that diffusion should occur at 1000°C in 1000 to 10000 sec, the experimental data did not confirm the results quantitatively. The data indicated that some diffusion had occurred in the desired direction but the gradient of nitrogen concentration in the original plate masked any quantitative results. At this time, it seems probable that the improvement expected from diffusing nitrogen from the weld zone will not justify the expense of extended experimental work in this direction.

The work done on the aging study of precipitates in the weld metal indicates that it may be possible to improve the properties of the material by post-weld heat treatment at 1200°C . However, the studies also indicate the presence of boundary precipitates at that temperature so that physical test data are needed to establish the best heat treating conditions.

Polygonization heat treatments have not progressed sufficiently to give any information on the value of this method of obtaining a fine grain effect.

The use of Zr as a deoxidizer for vacuum sintered molybdenum showed only moderate success since the material tended to form hot cracks as indicated by the low melting point of Zr as compared to molybdenum. The ductility of the Zr deoxidized vacuum sintered material compares favorably with carbon deoxidized arc-cast molybdenum. It was found that mixing Ti powder with molybdenum powder in an acetone slurry was not successful in improving either the homogeneity or the welding properties since the weld samples showed segregation and porosity.

VI CONCLUSIONS

The following conclusions were drawn from the work with purified welding atmospheres:

- (1) It is possible to make fusion welds in which the oxygen and nitrogen concentrations are not increased over that of the original plate through the use of purified argon or helium.
- (2) The improvement obtained in carbon deoxidized arc-cast molybdenum when welded under purified argon or helium is relatively small as compared to the effects of some alloying elements.
- (3) Purified argon and helium are recommended for welding applications because of the possible variation in commercial inert gases, and the loss of ductility when the welding atmosphere contamination exceeds relatively close limits.

The following conclusions were drawn from the work with arc-cast molybdenum deoxidized with different materials:

- (1) In carbon deoxidized molybdenum, the ductility is improved by increasing the carbon content from 0.04% to 0.06%.
- (2) The addition of 0.5% Ti increases the ductility of arc-cast molybdenum so that weld metal may be bent 120° at 80°F when welds are made in 0.05% carbon material under purified argon.
- (3) Increasing the carbon content of molybdenum deoxidized with 0.5% titanium improves the ductility in the range 0.015% to 0.05% carbon.

- (4) The use of aluminum as a deoxidizer in the amount 0.16% with 0.01% carbon produced welds which could be deflected 120° at 140°F.

The work with residual welding stresses resulted in the following conclusions:

- (1) The stresses in the region of the weld crater are of the same order as the stresses required for rupture at room temperature.
- (2) The use of thermal treatment as a post-welding stress relief should be investigated.
- (3) The molybdenum used for welding applications should have sufficient strength and ductility to prevent the formation of cracks until the material could be thermally relieved.
- (4) Welded design for molybdenum joints should consider the values of thermal stresses involved.

The work with nitrogen diffusion from the weld metal led to the following conclusions:

- (1) There seems to be qualitative and theoretical value in the removal of nitrogen from the weld metal by diffusion.
- (2) The data obtained were inconclusive as to quantitative values of the diffusion constants for nitrogen diffusion from molybdenum weld metal into the parent plate.

Studies on thermal treatment of molybdenum weld metal indicated the following:

- (1) Precipitates found in the as-welded material may be removed by heating the weld metal at temperatures in excess of 1600°C for one hour.

The studies with vacuum sintered molybdenum yielded the following conclusions:

- (1) The deoxidization technique used in the preparation of Ti deoxidized sintered molybdenum is critical as to the means used to protect the Ti powder prior to the sintering operation. Thus far, water seems to be the best protective agent.
- (2) The use of Zr as a deoxidizer shows some possibilities and should be investigated further.

VII RECOMMENDATIONS

The work on welding atmospheres shown in this report indicates that further purification of the welding atmosphere will show relatively little improvement over the results obtained at the present state of the investigation. It is recommended that further studies in this direction be discontinued. However, it is suggested that welds in future investigations be made in purified argon to avoid the possibility of excessive contamination.

The work on deoxidizing and alloying additions to the molybdenum showed that considerable improvement could be obtained through the use of proper alloy additions. The future investigations should be directed toward the development of a molybdenum alloy which is designed for welding. Such an alloy would have to be properly deoxidized and the work thus far indicates that the recrystallization temperature should be high and the rate of grain growth low. These characteristics should give a minimum grain size in the weld metal and take advantage of the grain size effect on impurity concentration.

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